

Catalytic Effect of Iron on the Carbon-Carbondioxide Reaction Kinetics

By

Varun Kumar Sinha

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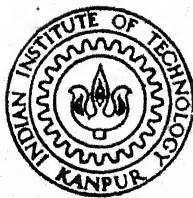
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DEPARTMENT OF METALLURGICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

JULY, 1979

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A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY

By
Varun Kumar Sinha

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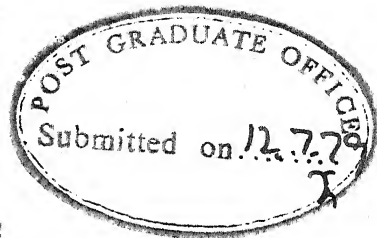
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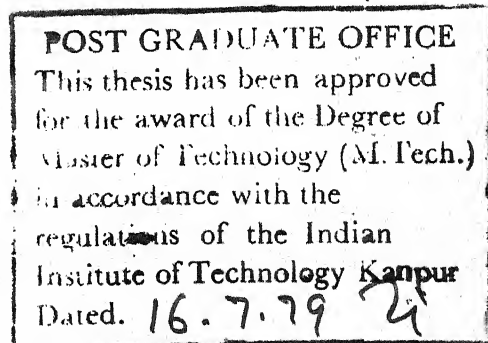
CERTIFICATE

This is to certify that this work "CATALYTIC EFFECT OF IRON ON CARBON-CARBON DIOXIDE REACTION KINETICS" has been carried out by Mr. Varun Kumar Sinha under my supervision and has not been submitted elsewhere for award of a degree.

DR. S.P. MEHROTRA

Assistant Professor
Dept. of Metallurgical Engineering,
Indian Institute of Technology,
Kanpur-208016

IIT Kanpur
July 12, 1979.



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Varun Kumar Sinha

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ABSTRACT

The kinetics of carbon-carbon dioxide reaction (at 1 atmosphere) and the catalytic effect of iron on this reaction was studied at several temperatures in the range 850 to 1000°C. The activation energy corresponding to the overall rate of the reaction was found to be 65.7 kcal/gm mole, which is lower than the activation energy for the gasification reaction (~ 80 kcal/gm-mole) and higher than the activation energy for the transport step (~ 45 kcal/gm mole). From the activation energy value it is, thus, evident that both the transport of gas through the pores and the gasification reaction at the pore surface contribute to the overall rate. Using the concept of effectiveness factor the intrinsic rate values for gasification reaction at various temperatures were evaluated. The activation energy corresponding to the intrinsic rates was found to be 75 kcal/gm-mole, which is close to the activation energy values reported in the literature.

The catalytic effect of iron on the C-CO₂ reaction was investigated for varying amounts of iron ranging from 1 to 15 per cent by weight. It is observed that the rate of gasification reaction increases with increasing iron content in the compacts. Qualitatively the rate at a given temperature seems to increase linearly with increasing iron content. Activation energy for reaction decreases with increasing iron content. It is noticed that the reduction in activation energy is rapid for initial additions of iron and then decreases linearly with further addition of iron beyond 1%.

CHAPTER - I

CHAPTER I

INTRODUCTION

Carbon-carbon dioxide reaction is becoming more and more important as new applications of carbon as high temperature material, as a moderator in nuclear reactors or a construction material for electrode, certain parts in rocket, ram jets, turbine, etc., are being found. In all these applications, however, oxidation limits the usefulness of the material. It is now established that the rate of $C-CO_2$ reaction controls the overall kinetics of reduction of hematite by carbon^{1,2}. This reaction has also been found to critically affect the overall rates of generation of watergas and production of producer gas.^{3,4}

It is now an accepted fact that the presence of impurities in carbon affects the kinetics of $C-CO_2$ reaction to a very large extent. The study of influence of solid catalysts on gasification of carbon by oxidizing gases like O_2 , CO_2 and H_2O has evoked extensive investigations. In general, the presence of transition elements have been found³⁻⁷ to produce good catalytic effect on gasification of carbon. Amaglio⁸ and Thomas & Walker⁹ observed that silver, manganese and barium are even better than transition metals as catalyst. Oxides and salts of alkali and alkaline earth metals have also been reported to have catalytic effect on $C-CO_2$ reaction.^{3,6,7,10-13} Even certain noble metals of colloidal dimension have been reported to act as good oxidation catalyst.^{6,9,14-17} It is therefore more or less established

that the purified carbon oxidizes at a lower rate.^{10,18,19} Thus, a knowledge of catalytic effect of impurities on the reactivity of carbon could be of crucial importance for both types of applications of carbon, namely the ones in which the oxidation rate is to be enhanced, and the ones in which the oxidation rate is to be lowered.

Although a number of studies on catalytic effect of impurities on reactivity of carbon are reported in literature, it has not been possible so far to correlate the reactivity of carbon with the concentration of impurities present in the material mainly due to the fact that different impurities have varying effects on the oxidation behaviour of carbon which itself may be of various kinds, e.g., graphite, charcoal, electrode carbon, coke etc. and also the oxidizing atmosphere may be of different types.

In the present investigation ^{an} attempt has been made to study the kinetics of the reaction of porous pellets of carbon with carbon dioxide in the temperature range 850 to 1000°C. The effect of varying concentration of iron powder in the porous pellets, ranging from 1 to 15 per cent by weight, on the kinetics of C-CO₂ reaction in the above mentioned temperature range is studied. An attempt has been made to atleast qualitatively correlate the rate of C-CO₂ reaction with the concentration of iron impurity in carbon.

CHAPTER - II

CHAPTER II

LITERATURE REVIEW

A very large number of studies on various aspects of carbon-carbon dioxide reaction are available in literature. It is, however, neither possible nor necessary to review all these publications. Instead, only those concerned with the basic aspects related to the kinetics and the catalytic effect of iron on this reaction have been reviewed in this chapter. For convenience the review is done under two main headings: (1) kinetics of the uncatalyzed reaction between carbon and carbon dioxide, and (2) catalytic effect of iron on the kinetics of C-CO₂ reaction.

2.1 KINETICS OF UNCATALYZED REACTION BETWEEN CARBON AND CARBON DIOXIDE

The reaction of carbon dioxide with carbon is a heterogeneous reaction in which the solid carbon itself is consumed. The reaction takes place not only on the outer surface of the carbon compacts but also in the interior due to penetration of carbon dioxide into the porous carbon mass. Although the bulk gas phase is composed entirely of carbon dioxide it is obvious that the gas phase within the interior of the carbon compacts will be a mixture of the reactant gas CO₂ and the product gas CO. Any interpretation of the data must, therefore, recognise the fact that inside

the pores the gasification of carbon will be taking place in CO_2 and CO gas mixture.

2.1.1 Mechanism of the Reaction

The stoichiometric equation $\text{CO}_2 + \text{C} = 2 \text{CO}$ only gives the overall reaction and fails to reveal the mechanism of the reaction. To find out the mechanism of the reaction Rao and Jalen²⁰ identified the following seven successive steps involved in the C-CO_2 reaction:

1. Transport of CO_2 to the exterior surface of the carbon pellet.
2. Diffusion of CO_2 into the interior of the porous pellet, viz., pore diffusion of reactant.
3. Chemisorption of CO_2 on the pore surface as well as on the external surface.
4. Surface reaction.
5. Desorption of CO , the product of reaction.
6. Outward diffusion of CO from the interior of the pellet, viz., pore diffusion of product.
7. Transport ^{of} CO from the surface of the pellet into bulk-gas phase. Step 3, 4 and 5 deal with the chemical aspects of the reaction and 1, 2, 6 and 7 are physical or transport steps.

It is to be expected that at low temperature the kinetics of the reaction would be chemically controlled. The transport of CO_2 and CO between the reaction sites as the pore surface

and the bulk gas phase proceeds relatively rapidly. The gas composition in the pores within the pellets would be uniform and have a value close to that of the bulk gas phase.

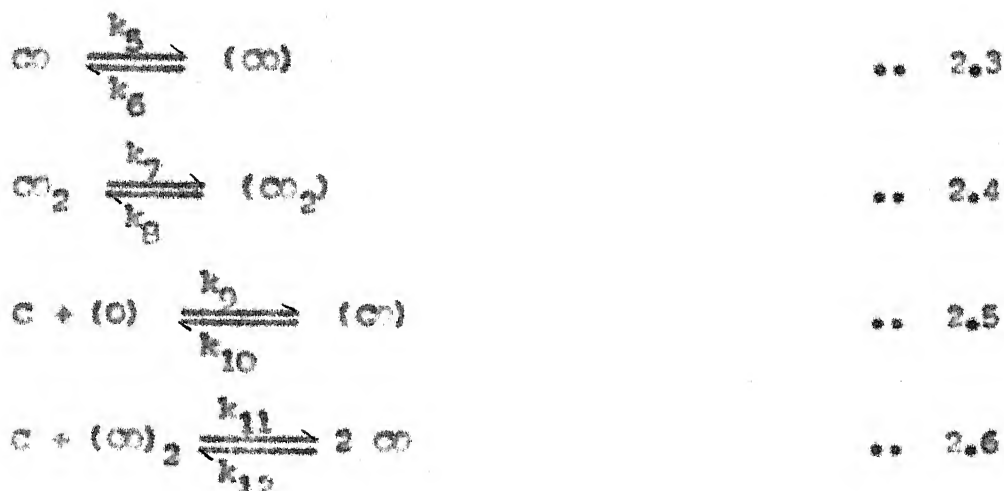
At higher temperatures, however, the transport steps 2 and 6 can no longer be considered negligible. This is due to the fact that with increasing temperature the rate of a chemical step increases very rapidly. The corresponding increase in the rates of the transport steps is somewhat limited. Thus the chemical and transport steps proceed at comparable rates.

At still higher temperatures the chemical steps occur at extremely high rates and thereby cease to be the rate controlling step. At these temperatures film diffusion steps 1 and 7 may play an important role.

The earlier investigations²²⁻²⁵ have established that the kinetics of $\text{O}-\text{CO}_2$ reaction except under specific experimental conditions is significantly controlled by transport steps.

In a critical review of early work (upto 1952) on $\text{O}-\text{CO}_2$ reaction Reif²¹ recognised that the mechanisms and rate expressions for this reaction given by his predecessors could be arrived at using some combinations of some of the following six reactions:





The bracketed terms denote chemisorbed species.

TABLE 2.1

Group of Investigators and C-CO₂
Rate Equations used by them²¹

Group of Investigator	Equations Used
Smeklova et al. ²⁶	2.1, 2.2, 2.4
Gadsby et al. ²⁷	2.3, 2.4, 2.6-fwd.
Gadsby et al. ²⁸	2.1-fwd, 2.2-fwd, 2.3
Key ²⁹	2.1, 2.2
Wu ³⁰	2.1-fwd, 2.3, 2.5-fwd

Table 2.1 given by Reif²¹ identifies the groups of workers²⁶⁻³⁰ and the equations used by them to propose their kinetic models. Reif²¹ proposed a two step mechanism for C-CO₂ reaction in which in the first step the forward and reverse reaction of Eq. 2.1 are supposed to occur rapidly so that equilibrium is established between the carbon surface and the gas phase consisting of CO₂

and CO. In the second step the forward reaction of Eq. 2.2 is considered to proceed slowly and its rate determines the overall rate of C-CO₂ reaction.

The two observations that a small amount of carbon monoxide mixed with carbon dioxide greatly reduces the rate of C-CO₂ reaction²⁸⁻³¹ and that carbons chemisorb oxygen at certain surface sites^{26, 28, 33-35} are now widely accepted. In Reif's mechanism²¹ the effect of carbon monoxide is accounted for by the reverse reaction of Eq. 2.1. Increase in carbon monoxide content in the gas phase decreases the surface sites covered by chemisorbed oxygen. Gadsby and coworkers,²⁸ however, attributed the inhibiting effect of carbon monoxide to the strong chemisorption of carbon monoxide



which according to them lowers the fraction of sites occupied by chemisorbed oxygen. This conclusion however, was contradicted by the experimental findings of Strickland & Constable³⁶ and Reif.²¹ The postulate of the Reif's mechanism²¹ have found further support from Bryun and coworkers,^{33, 34} Grabke³⁵ and others.³⁷⁻³⁹ Combining the principle of conservation of total number of reaction sites on carbon surface Bryun³³ reformulated the mechanism of C-CO₂ reaction as follows:



where f_c and $(O)_c$ denote free and occupied reaction sites, respectively, on the carbon surface. Grabke,³⁵ however used the concept of stationary oxygen activity, a_o , on the carbon surface in preference to the conserving the total number of reaction sites. Using a two step mechanism very much similar to that of Reif²¹ he observed that the rate was directly proportional to the oxygen activity on the graphite surface.

Turkdogan and Vinters⁴⁰ proposed a mechanism which is different from that of Reif,²¹ Brown et al.,^{33,34} and Grabke.³⁵ According to them⁴⁰ the reaction involves two steps. In the first step carbon dioxide gets dissociated on carbon surface.

Step 1:



This is followed by formation of carbon monoxide according to the following scheme:

Step 2:



According to this mechanism carbon monoxide inhibits the reaction first by covering the surface sites on carbon and secondly by decreasing the activity coefficient of $(CO_2)^{\#}$ in step 1.

2.1.2 Rate Expressions

Reif²¹ observed that the rate expression for C-CO₂ reaction proposed by earlier workers,²⁶⁻³⁰ could be described by a general

$$\text{Rate} = \frac{K_1 P_{\text{CO}_2}}{1 + K_2 P_{\text{CO}} + K_3 P_{\text{CO}_2}} \quad \dots 2.10$$

where P_{CO} and P_{CO_2} are partial pressures of CO and CO_2 respectively, and constants K_1 , K_2 and K_3 are functions of one or more rate constants which characterize Eq. 2.1 to 2.6. Assuming that the different steps of reactions can occur exclusively on carbon surface Eq. 2.10 could be derived on the basis of several combinations of certain of reactions 2.1 to 2.6. Using Arrhenius³³ formalism Rao and Jalen²⁰ derived a generalized rate expression which, they claim, would be valid under all experimental conditions:

$$r = k_e k_{el} [\text{C}] P_{\text{CO}_2} / (k_{el} P_{\text{CO}_2} + k'_{el} P_{\text{CO}_2} + K_{e2}) \quad \dots 2.11$$

They further showed that instead of Arrhenius³³ formalism if Grabke's³⁵ formalism is used the following rate expression would be obtained.

(1) At $P_{\text{CO}_2}/P_{\text{CO}}$ ratio less than 0.2

$$r_{e1} = k_{g2} (P_{\text{CO}_2}/P_{\text{CO}}) \quad \dots 2.12$$

(2) At $P_{\text{CO}_2}/P_{\text{CO}}$ ratio greater than 0.2

$$r_{e1} = k_{g2} (P_{\text{CO}_2}/P_{\text{CO}}) / [1 + K (P_{\text{CO}_2}/P_{\text{CO}})] \quad \dots 2.13$$

where k_{g2} is the forward rate constant for the reaction



Two different rate expressions to represent the rate data on the C-CO₂ reaction have been derived by Turkdogan et al.^{40,41}

(1) At P_{CO_2}/P_{CO} ratio less than 9.0

$$r_{t1} = \beta_1 [P_{CO_2} - P_{CO_2,e}] / [1 + P_{CO}/P_{CO_2}] \quad \dots 2.15$$

(2) At lower CO contents

$$r_{t2} = \beta_2 [P_{CO_2}]^{1/2} \quad \dots 2.16$$

Making correction for incomplete pore diffusion effects Rao and Jalan²⁰ interpreted their intrinsic rate values (rate free of mass transfer effects) using Ergun-mechanism. Using this mechanism they deduced the following rate equation:

$$\text{rate} = \frac{k_{e1} k_{e2} [IC] P_{CO_2}}{(k_{e1} P_{CO_2} + k_2)} \quad \dots 2.17$$

In pure CO₂ gas at 1 atm. pressure, the Eqn. 2.17 could be rewritten as

$$\text{rate} = \frac{k_{e1} k_{e2} [IC]}{k_{e1} + k_{e2}} = \frac{k_1}{1 + 1/I_3} \quad \dots 2.18$$

$$\text{where } k_1 = k_{e2} [IC] \quad \dots 2.19$$

$$\text{and } I_3 = k_{e1}/k_{e2} \quad \dots 2.20$$

Rao and Jalan²⁰ have critically examined the similarities between various rate expressions.

$$I_1 = k_{e1} [2C], \quad I_2 = k'_e / k_{e2}$$

$$\text{and } I_3 = k_{e1} / k_{e2} \quad \dots 2.21$$

Eq. 2.11 could be rewritten as

$$Y_E = I_1 P_{CO_2} / (1 + I_2 P_{CO} + I_3 P_{CO_2}) \quad \dots 2.22$$

As reported by Weis,²¹ the experimental data of Wu,³⁰ Rey,²⁹ Gadsby et al.^{27,28} and Simechkova et al.²⁶ satisfy the Eq. 2.22 . Rewriting Eq. 2.18 in the following form

$$Y_E = (I_1/I_2) (P_{CO_2}/P_{CO}) / \left[1 + \left(\frac{I_3}{I_2} \right) \left(\frac{P_{CO_2}}{P_{CO}} \right) \right] \quad \dots 2.23$$

Rao & Jalan²⁰ noticed strong resemblance between Eq. 2.23 and Grabke's rate expression given by Eq. 2.13 , since I_3 and I_2 are intrinsic constants the ratio I_3/I_2 could be compared to K .

Rao and Jalan²⁰ further showed that Turkdogan et al.⁴⁰ rate expression (Eq. 2.15) could also be deduced from Eq. 2.22 . Under conditions of complete pore diffusion the gas composition could be uniform throughout the carbon sample and equal to that of the bulk gas phase. Assuming CO_2 -CO gas mixture at a total pressure of 0.96 atm. Eq. 2.22 could be modified as

$$Y_E = \left[\frac{I_1}{1 + 0.96 I_3} \right] P_{CO_2} / \left[1 + (I_2 - I_3) / (1 + 0.96 I_3) P_{CO} \right] \quad \dots 2.24$$

Taking P_{CO} term in Eq. 2.15 as $(1 + 0.96 I_3) / (I_2 - I_3)$ Rao & Jalan²⁰ observed that Eqs. 2.14 & 2.15 could be compared

when P_{CO_2} is negligible (which is true at high temperatures).

2.2 CATALYTIC EFFECT OF IRON ON C-CO₂ REACTION

A large number of studies^{3,5,9,13,16,19,42-46,48-52} have been carried out to investigate the effect of iron and its compounds on C-CO₂ reaction. It has been a point of controversy whether free metal, oxide, carbide or any other salt produces best catalytic effect.

Gulbransen & Andrew⁴⁵ found that at 850°C and 10^{-6} mm Hg pressure the rate of reaction of C with CO₂ was increased 830 times by addition of 0.079% iron when compared to that of iron free sample. Turkdogan and Vinters⁵³ studied the effect of iron (<0.01 to 2.1%) at 700-1000°C and 0.03 to 1.0 atm. pressure, and found that with 2.1% Fe the rate of oxidation in CO₂ is a factor of 10^6 greater than that of Fe-free graphite. After 20 to 50% oxidation the catalytic effect of iron diminishes. Gralke,⁴² and Ravona¹³ have also observed the catalytic effect of iron on C-CO₂ reaction. Follet,⁵⁰ found that iron becomes more active catalyst in presence of single vacancy in $\{0001\}$ of graphite, than in the absence of such vacancy. Sykes & Thomas⁵⁴ studied the catalytic effect of iron as a function of concentration of iron for very low concentrations and reported an increase in the rate of C-CO₂ reaction with increasing iron content. King and Jones¹⁹ observed that initial reactivity of coke was proportional to the amount of "reducible iron" present (reducible iron means

the iron reducible to metallic state or already present in metallic state). They¹⁹ found that if the reducible iron was rendered non-reducible the reactivity decreased and vice-versa.

2.2.1 Effect of Iron oxide and other Iron compounds

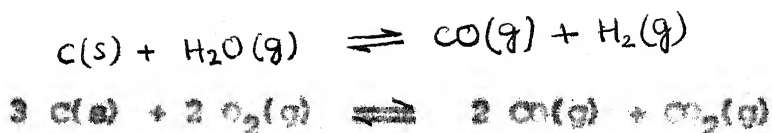
Effect of iron oxide as a catalyst has also been reported by a large number of investigators.^{3,6,11,43-45,48,49} Tuddenham and Will⁵ reported an increase in reactivity by a factor of 32 by addition of about 0.025% iron-oxide at 1100°C. A weight loss of 30% in less than one hour at 600°C with 5% ferric oxide was reported by Holmes and Emmett,⁴⁸ whereas without ferric oxide no loss in weight was observed. Roy et al.,^{43,44} Blayden et al.,⁴⁹ Thomas,¹⁶ Thomas & Walker⁹ have reported slight catalytic effect of iron oxide on C-CO₂ reaction. But Taylor and Neville³ and Gulbransen & Andrew⁴⁵ observed practically no catalytic effect of iron oxides on C-CO₂ reaction.

Ferric chloride and ferric citrate have also been reported^{46,51} to have some catalytic effect on C-CO₂ reaction.

2.2.2 Mechanism of catalysis

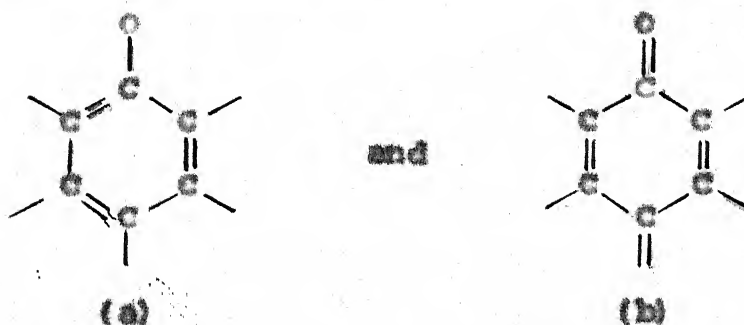
Earlier it was thought^{4,6,56-59} that the catalytic action in C-CO₂ reaction was due to formation of intermediates, which served to oxidise carbon in their vicinity and in this process they returned to their original state only to be reconverted by the oxidising gas to the active intermediate.

About a quarter century ago evidence had accumulated to suggest that the intermediate compound theory might be erroneous for a number of reasons. Long and Sykes^{18,60,61} in their detailed study of the effect of specific catalysts on the reactions

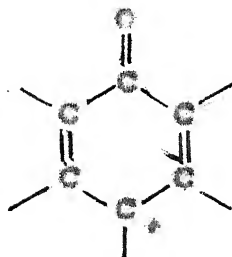


concluded that the general course of gasification process did not appear to be modified by the catalytic impurities. There were also other factors which seemed inexplicable in the terms of the intermediates added to purified carbons interacted with the oxidizing gases to a much greater extent than the originally present natural impurity in carbon did.⁶¹ Long and Sykes⁶¹ formulated their electronic theory to explain the mechanism of the catalysis.

When oxygen atom is absorbed at an active site on the carbon surface, two types of distribution of π -electrons may be schematically represented:

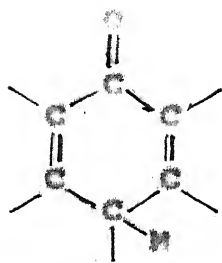


Of the above two structures (b) is more favourable for the evolution of carbon monoxide, because carbon-carbon bonds which must be broken are weaker and carbon-oxygen bond approximates more closely to that in the carbon monoxide molecule. Structure (b) can be derived from (a) by transfer of an electron from the carbon to a transition metal ion



or,

by the formation of a covalent bond with an alkali metal ion M.



The mobility of π -electrons provide a means by which catalysts situated at various points in or on the graphite lattice can influence events at active sites. Using molecular orbital theory Long & Sykes¹⁸ found that the change in bond strength by such electronic rearrangements are of a significant magnitude. The electronic theory has helped to put the modes of action of various specific catalysts into rational perspective. Under certain circumstances^{22, 59, 60} it offers a logical interpretation of the observed phenomena. Experimental results of Rakaszewski⁵² also supports this theory. In early sixties the work of Duval,⁶² Heuchamps,⁶³ Amareglio⁶ etc. once again supported intermediate compound theory.

The results of Henning,¹⁴ Newson¹⁵ and others^{6, 9, 16, 17} show that many metals including certain noble ones of colloidal dimensions, can act as extremely good oxidation catalysts. Henning¹⁴ and Duval,⁶⁴ both have observed that the catalytic

activity depends upon the particle size of the metal catalyst, this has been explained on the basis of 'Kobsev theory of ensembles'.

Thomas¹⁶ and Thomas & Walker⁹ have observed that catalytic pitting of the basal $\{0001\}$ planes of graphite crystals is progressively diminished as the iron particles gradually become oxidized. Thus oxide can not be the most effective form of catalyst. But still, nothing conclusively can be said free metal or carbide being the most effective form of catalyst. For, it may be that a thin layer of non-stoichiometric oxide is the dominating factor. And when the non-stoichiometry is destroyed there will be no catalysis.

The knowledge of the nature of the crystalline imperfection with which the catalysis interact, and the chemical state of catalytic impurity is becoming important as the lattice defects in graphite^{65,66} and radiation damage¹⁶ modify the pattern of catalysis. In the presence of single vacancy in $\{0001\}$ planes of graphite, iron is a much more active catalyst than in the absence of such a vacancy.⁵⁰

Although nothing conclusively can be said about the acceptability of one theory over other, the intermediate compound theory is rather being more favoured these days. There are two major points which go against the electronic theory: (i) experimental evidence seems to suggest that the activation energy of oxidation is independent of concentration of the catalyst and (ii) the metals that seem to be most active catalysts are capable of forming higher oxides, which are reducible to lower

oxides or metallic state by carbon.⁶⁴ At the same time Henning^{14, 67} reports that from the observed motion of catalyst particles, as they channel across the graphite surface bonds are formed between the catalyst and a number of reactive carbon atoms at the carbon-metal interface, as proposed by Long and Sykes.⁶¹

Harker,⁶⁸ Harker and Gailer⁶⁹ are of the view that each catalytic system must be considered separately, because with a given catalyst the nature of active form depends upon which oxidation reaction is occurring.

CHAPTER - III

CHAPTER III

EXPERIMENTAL PROCEDURE

The experiments that were performed during the course of this investigation can be classified in the following two categories:

(1) The pellets of pure carbon were reacted with carbon dioxide at different temperatures, namely 850°, 875°, 900°, 925°, 975° and 1000°C. The data thus obtained served as the reference for studying the effect of iron on the reaction kinetics of C-CO₂ reaction.

(2) In the second category of the experiments, the carbon pellets, containing varying amounts of iron in them (1, 2, 5, 7.5, 10 and 15 per cent by weight) were reacted with CO₂ at the same temperatures as in category (1).

The experiments consisted of recording weight loss in the carbon pellets of different compositions, as they reacted with carbon dioxide gas at atmospheric pressure and fixed temperatures.

3.1 DESCRIPTION OF THE APPARATUS

The schematic diagram of the experimental set up has been shown in Fig. 3.1. It consists of a Kanthal wire wound vertical tube furnace. A 2.0 inch I.D. alumina tube served as the reaction chamber. A 5" long equi-temperature zone was maintained

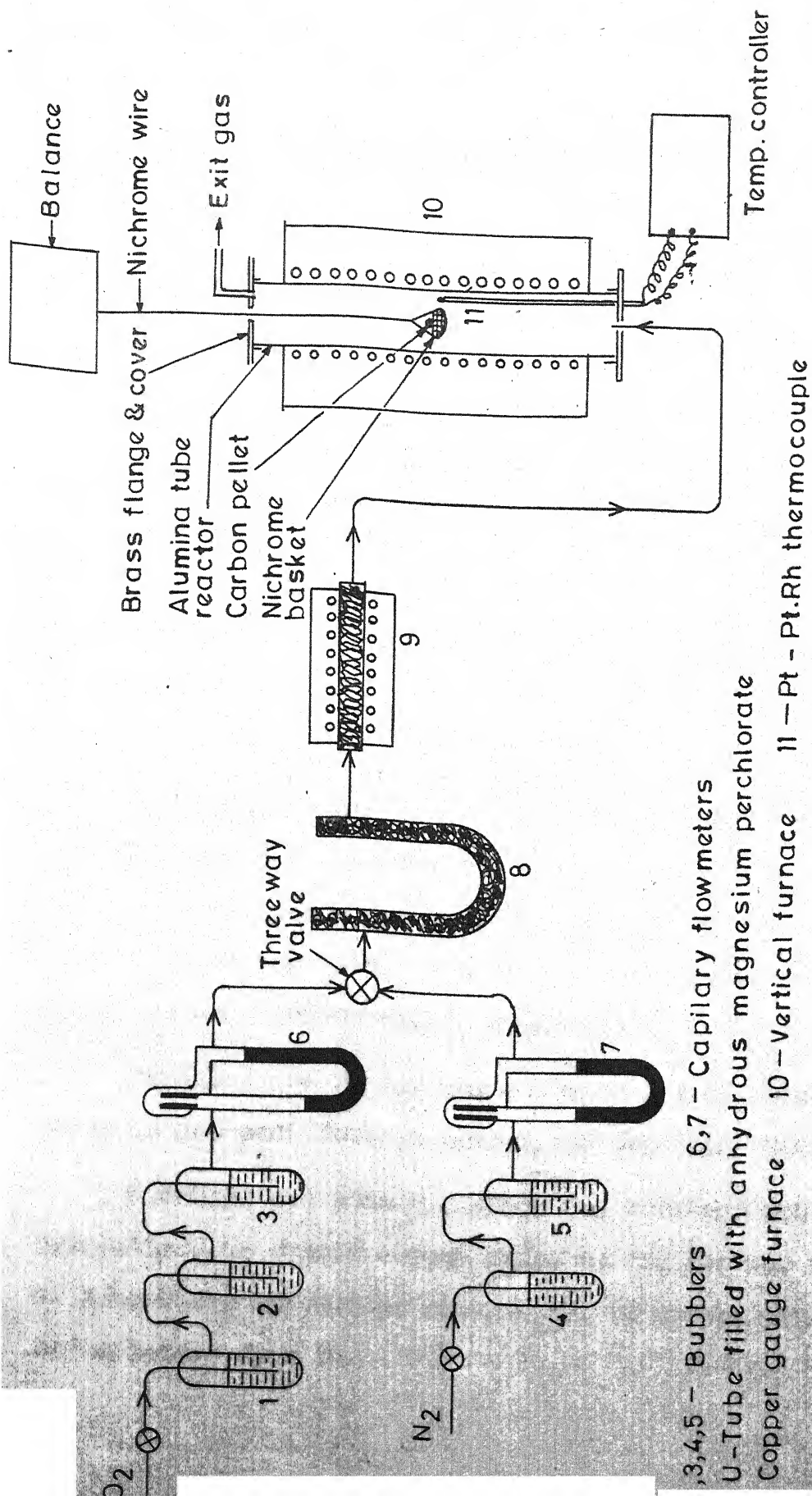


FIG.3.1 SCHEMATIC DIAGRAM OF EXPERIMENTAL SET-UP

at the centre of the furnace. Both ends of the alumina tube were open and connected brass flanges, which could be connected and tightened to brass covers with the help of nuts and bolts. Bottom cover had two holes, one for the gas inlet and the other for introducing the thermocouple. Top cover also had two holes one served as the outlet for the gases from the reaction chamber, and the other small hole at the centre for introducing the nichrome wire through which the pellet was suspended.

The temperature of the furnace was accurately controlled ($\pm 2^\circ\text{C}$) with the help of "Leads & Northrup Electronax" temperature controller using Pt-90% Pt, 10% Rh thermocouple.

'Sartorius' single pan balance was used to record weight loss of the pellet as of function of time. The balance was fixed on a platform about 3 feet above the verticle furnace.

A nichrome wire basket which contained the pellet was suspended into the reaction chamber with the help of a nichrome wire whose other end was connected to the single pan balance. The length of the nichrome wire was so adjusted to keep the basket in the equi-temperature zone.

Flushing gas H_2 and the reaction gas CO_2 were passed through separate gas purification trains and capillary flowmeters.

Nitrogen was passed through two bubblers containing alkaline pyrocellulose, to absorb oxygen where as CO_2 gas was passed through a of 3 bubblers containing conc. H_2SO_4 to remove organic impurities and moisture from it.

The volumetric flow rate of the flowing gas could be measured with the help of capillary flow meter. Outlets of the flow meters were connected to a three way valve. The third end of the valve lead to a U-tube filled with anhydrous magnesium perchlorate, followed by a copper gauge furnace kept at 500°C , to absorb moisture and oxygen, respectively. The purified gas was led into the reaction chamber from the bottom.

3.2 MATERIALS USED

Carbon was obtained from Thermoatomic Carbon, U.S.A. It has 99.91% fixed carbon and ash content less than 0.09%. Average particle size was < 5 microns.

Bentonite with average particle size 15 microns was used as binder.

Iron powder with 99.9% purity and average particle size 8 microns was used as catalytic impurity.

3.3 PREPARATION OF PELLETS

For every composition weighed amounts of carbon, bentonite and iron were thoroughly mixed with the help of a mortar and pestle. About 8% by weight, water was added and thoroughly mixed. Cylindrical pellets of $1/2$ " diameter were then pressed in a die at 6000 psi. The weight of each pellet was kept around 1.1 gm. Pellets were dried in an oven at about 150°C for about

16 hours. Pellets were stored in plastic containers properly labelled.

3.4 DETERMINATION OF POROSITY OF PELLETS

Porosity of a compact is defined as the ratio of volume of pores and volume of the compact. Mathematically it can be expressed as

$$\text{porosity, } P = 1 - \frac{\text{Apparent density of the compact}}{\text{True density of the powder}}$$

Apparent density of the compact was determined by weighing the specimen and determining the volume of the compact from its physical dimensions. True density of the powder was determined by using a specific gravity bottle and a liquid of known density. A desiccator connected to a vacuum pump was used to evacuate air from the pores, so that the liquid could fill the air gaps.

5 measurements were taken and the average density of carbon powder was found to be 1.806 gm/cm^3 . Knowing the true density of the powder and apparent density of the compact, the porosity of the compact was determined, and was found to be 0.314.

3.5 EXPERIMENTAL TECHNIQUE

To start the experiment, the copper gauze furnace and the reaction furnace were slowly heated up to the predetermined temperature. After the temperature of the furnace stabilized, complete set up was flushed with nitrogen for about 10 minutes.

A weighed pellet was then kept in the nichrome basket which was introduced into the reaction tube from top. Nitrogen flow was resumed. Top cover was properly tightened and the pellet was slowly lowered into the reaction tube to avoid any thermal shock, till it came in the middle of the equi-temperature zone. The position of the balance and the length of nichrome wire was so adjusted that the basket containing the pellet was freely suspended inside the reactor tube furnace. After pellet had attained the desired temperature, carbon dioxide gas was let in the reaction chamber at a flow rate of 2 liter/min. At this flow rate of CO_2 , the partial pressure of CO in CO_2 stream, even for highest reaction rate, is very small. Hence the poisoning effect of CO on C- CO_2 reaction kinetics can be ignored.²⁰ The loss in weight of the pellet was recorded at regular intervals of time.

After the experiment was over the flow of CO_2 was stopped and the reactor was flushed with nitrogen. The pellet was slowly withdrawn from the reactor after removing the top cover.

The results of these experiments are reported and discussed in the following chapter.

CHAPTER - IV

CHAPTER IV

RESULTS AND DISCUSSION

The basic data consists of measuring weight loss of carbon compacts suspended in CO_2 atmosphere at regular intervals of time. As pointed out in the previous chapter also two categories of experiments are performed. In the first category of experiments compacts of pure carbon (free of iron) were reacted with CO_2 at seven different temperatures ranging between 850°C and 1000°C whereas in second category carbon compacts having varying amounts of iron (1 to 15%) were reacted with CO_2 at the same seven temperatures.

Initial weights of the pellets used in various experiments are given in Table IV.1.

The weight loss data for various experiments are reported in Tables A-1 to A-7 (Appendix I).

The experimental weight loss data was transformed into fractional carbon burn off values (F) using the relationship

$$F = \frac{\Delta W}{W_0} = 1 - \left(\frac{W}{W_0} \right)$$

where, ΔW = weight loss sustained by the carbon pellet during time interval, t ,

W = weight of the carbon in pellet at time t .

W_0 = initial weight of carbon in the pellet.

TABLE IV.1

Initial weight of the pellets (in grams)

% Fe composition	Temperature °C					
	890°	875°	900°	925°	950°	975° 1000°
0	1.109	1.123	1.110	1.127	1.110	1.117 1.004
1	1.081	1.54	1.130	1.076	1.081	1.103 1.097
2	1.081	1.156	1.053	1.089	1.166	1.053 1.118
5	1.224	1.181	1.203	1.192	1.185	1.065 1.117
7.5	1.097	1.111	1.136	1.072	1.053	1.058 1.113
10	1.166	1.179	1.130	1.108	1.123	1.107 1.142
15	1.093	1.090	1.095	1.094	1.066	1.061 1.047

Fractional weight loss of pure carbon compacts as a function of time at seven temperatures is shown in Fig. 4.1. Similar plots for carbon compacts having varying amounts of iron in them are shown in Figs. 4.2 to 4.4. Weight loss data for iron containing carbon compacts has also been presented in the form of plots of fractional weight loss for carbon compacts containing varying amounts of iron at fixed temperatures in Figs. 4.5 to 4.7.

4.1 KINETICS OF UNCATALYZED CARBON-CARBON DIOXIDE REACTION

4.1.1 Effect of Temperature

The effect of temperature on kinetics of this reaction is quite obvious from Fig. 4.1. For example the time required for 50% carbon burnoff was reduced from 350 minutes at 950°C (extrapolated value) to 160 minutes at 1000°C.

As pointed out by Rao and Jalan²⁰ the overall rate would reflect the combined effect of pore diffusion of CO_2 and its reaction with the pore surface. They have further noted that if the pore structure remains unchanged during the reaction. The weight loss per unit mass of carbon pellet would be directly proportional to the length of time interval for an infinitesimal weight loss

$$-\frac{dW}{W} \propto dt \quad \dots 4.1$$

$$\text{or, } -\left(\frac{dW}{W}\right) = R_c dt \quad \dots 4.2$$

where R_c is reaction rate per unit mass of carbon per unit time.

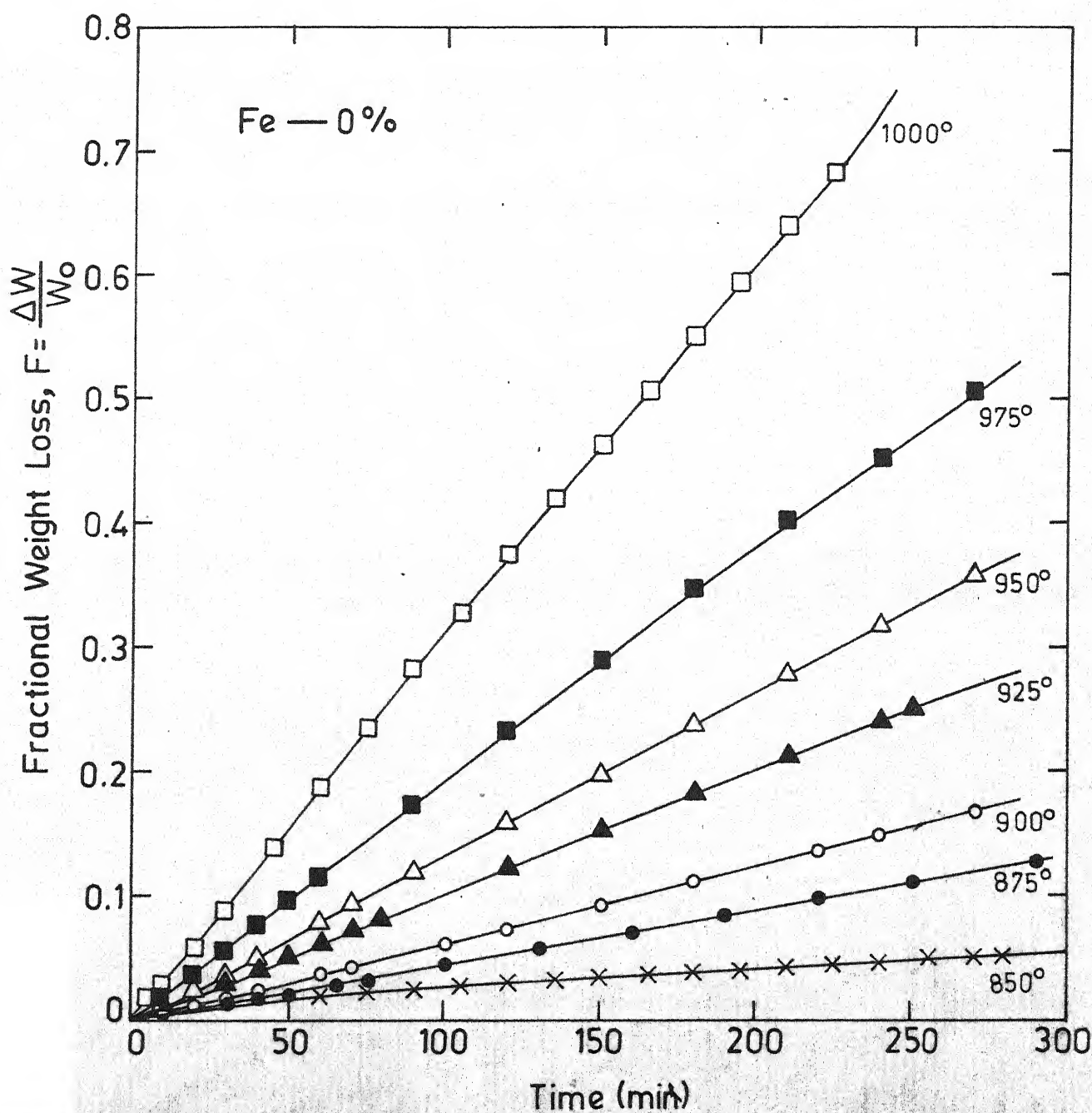


Fig.4.1. Plot of fractional weight loss as a function of time for iron-free carbon compacts at various temperatures.(°C)

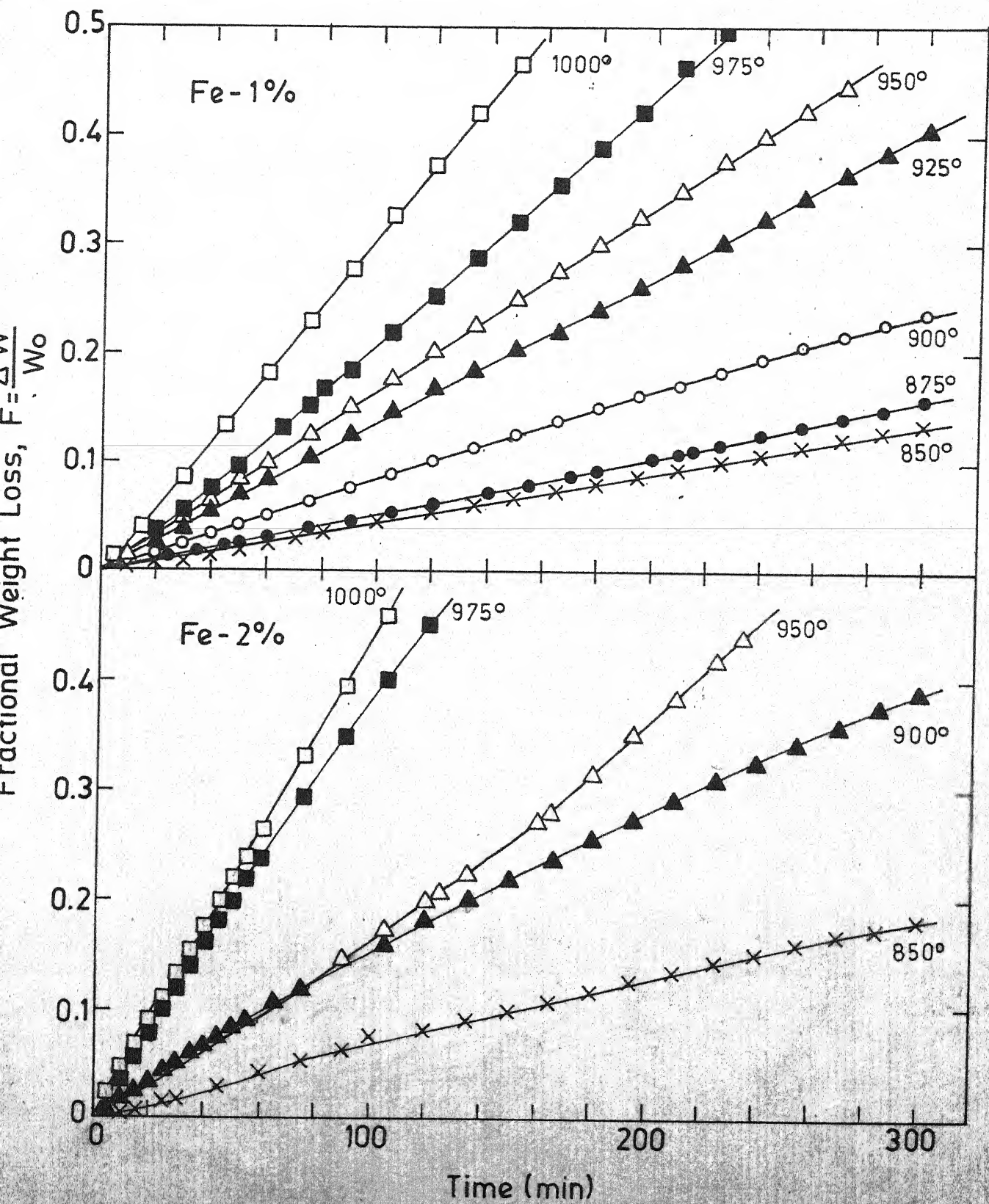
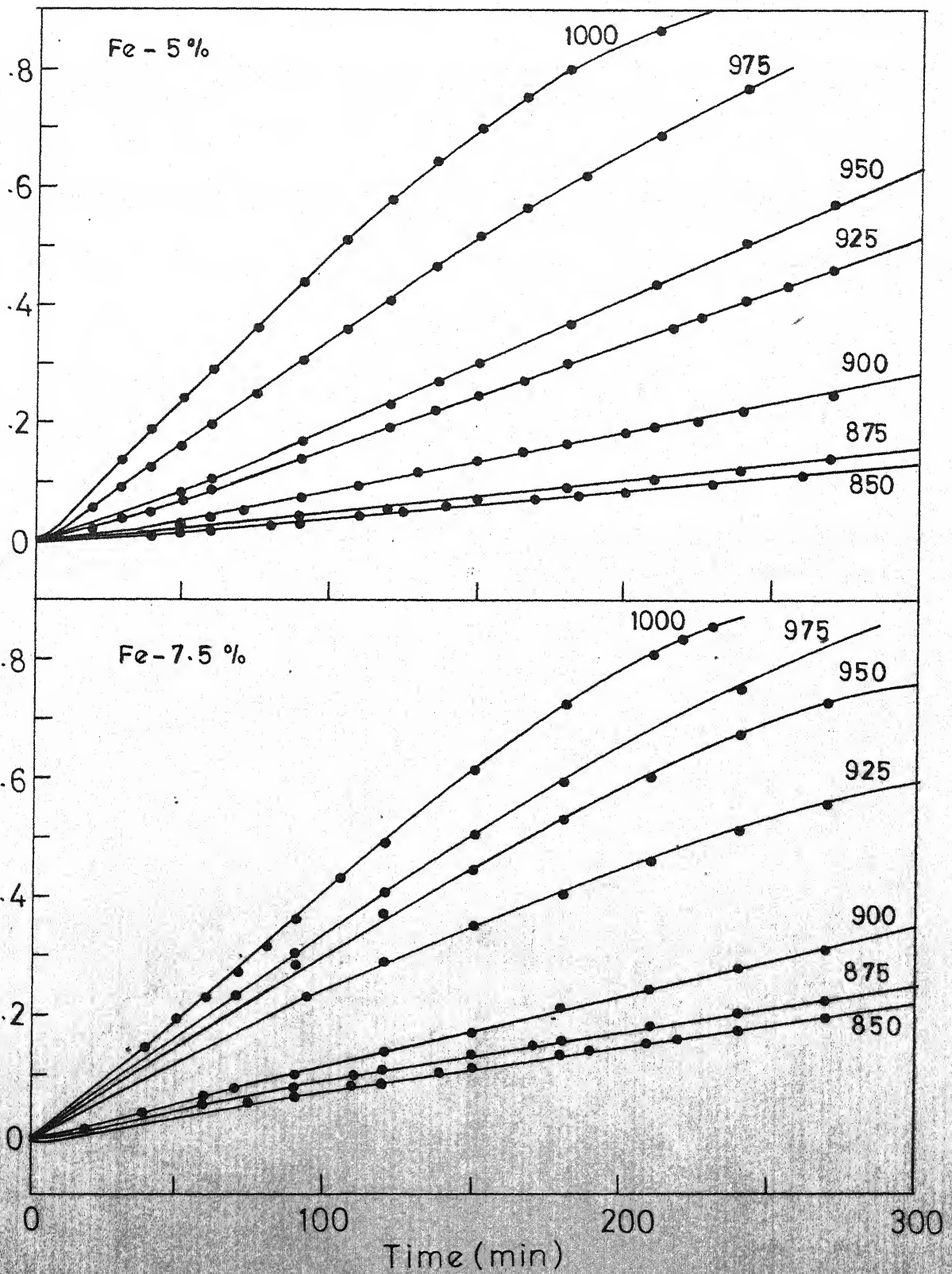


Fig. 4.2 Plot of fractional weight loss as a function of time for carbon compacts containing 1 and 2% iron, respectively, at various temperatures ($^{\circ}\text{C}$).



G.4-3 PLOT OF FRACTIONAL WEIGHT LOSS AS A FUNCTION OF TIME FOR CARBON COMPACTS CONTAINING 5 AND

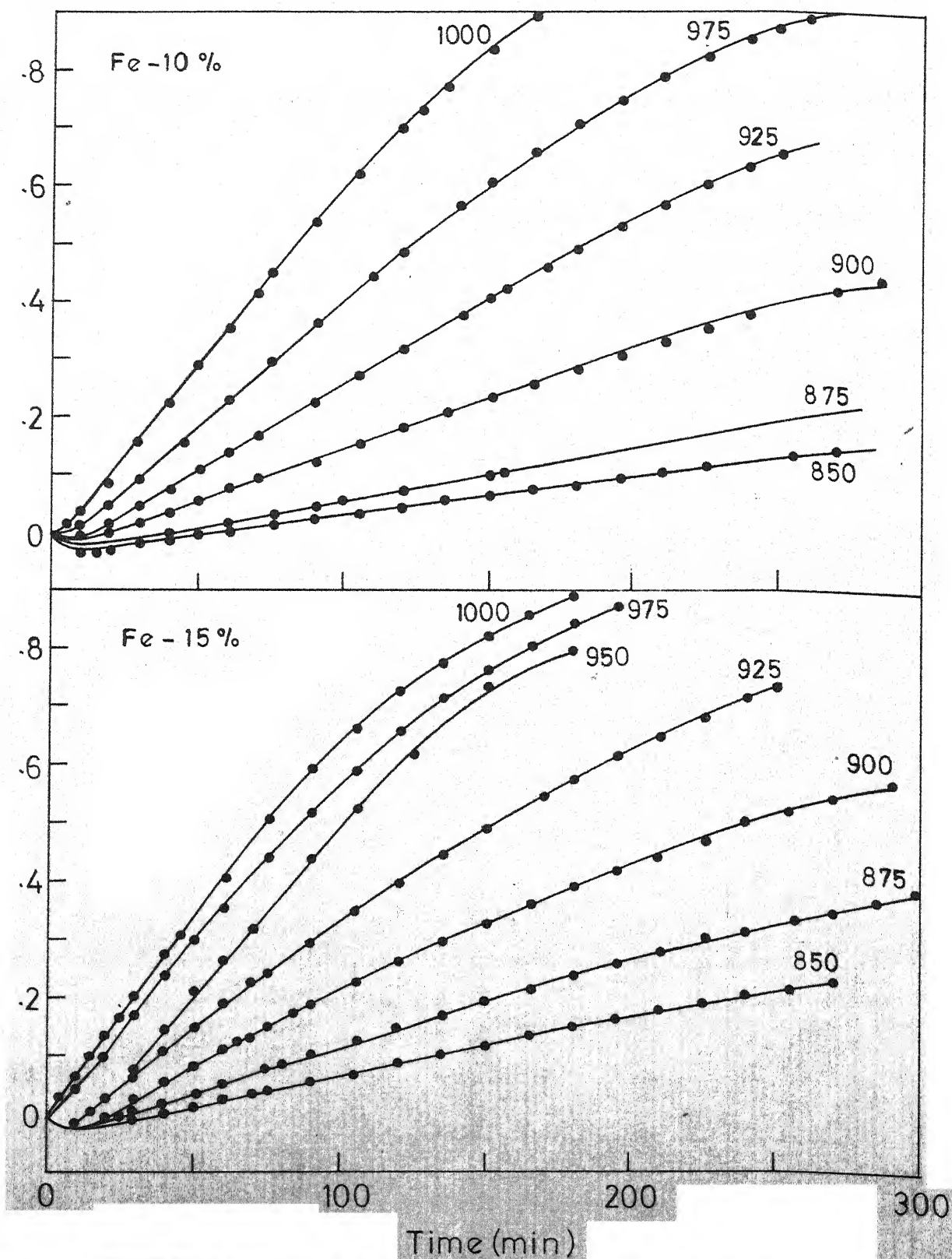
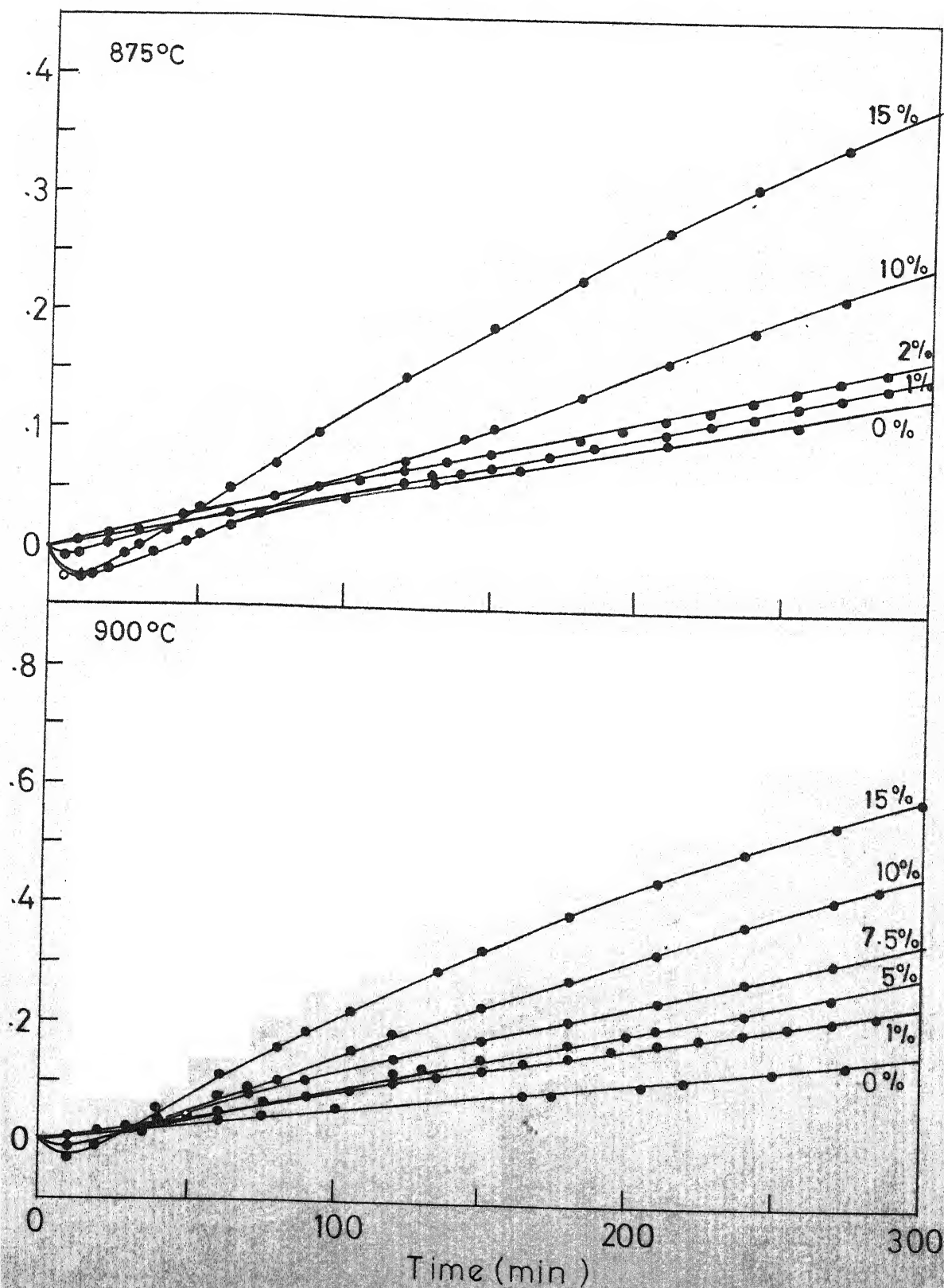
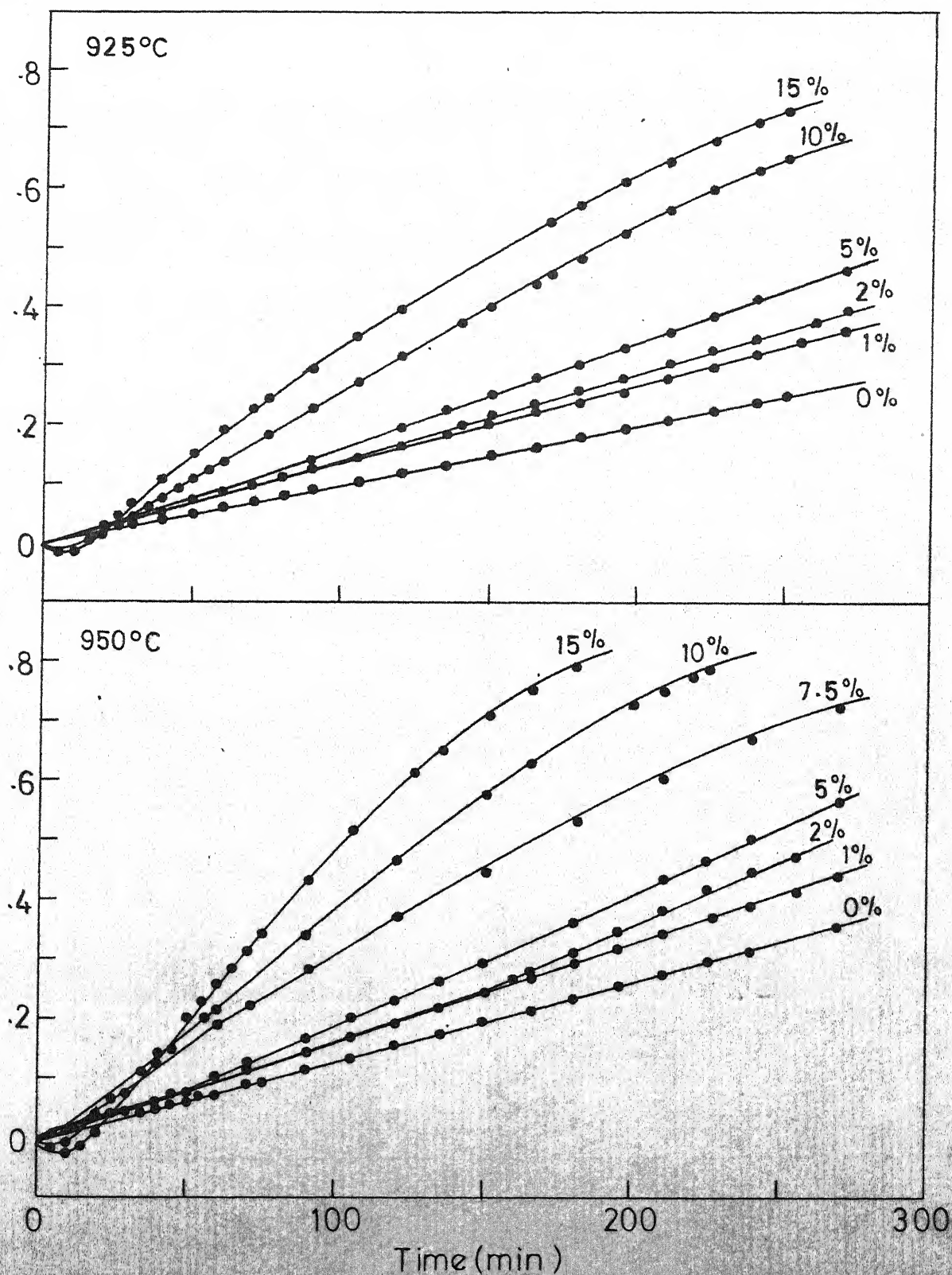


FIG. 4.4 PLOT OF FRACTIONAL WEIGHT LOSS AS A FUNCTION OF TIME FOR CARBON COMPACTS CONTAINING 10 AND 15% IRON FOR VARIOUS TEMPERATURES (°C)



4.5 PLOT OF FRACTIONAL WEIGHT LOSS AS A FUNCTION OF TIME FOR CARBON COMPACTS CONTAINING VARYING AMOUNTS OF IRON AT 875 AND 900°C



4.6 PLOT OF FRACTIONAL WEIGHT LOSS AS A FUNCTION OF TIME FOR CARBON COMPACTS CONTAINING VARYING AMOUNTS OF IRON AT 925 AND 950°C

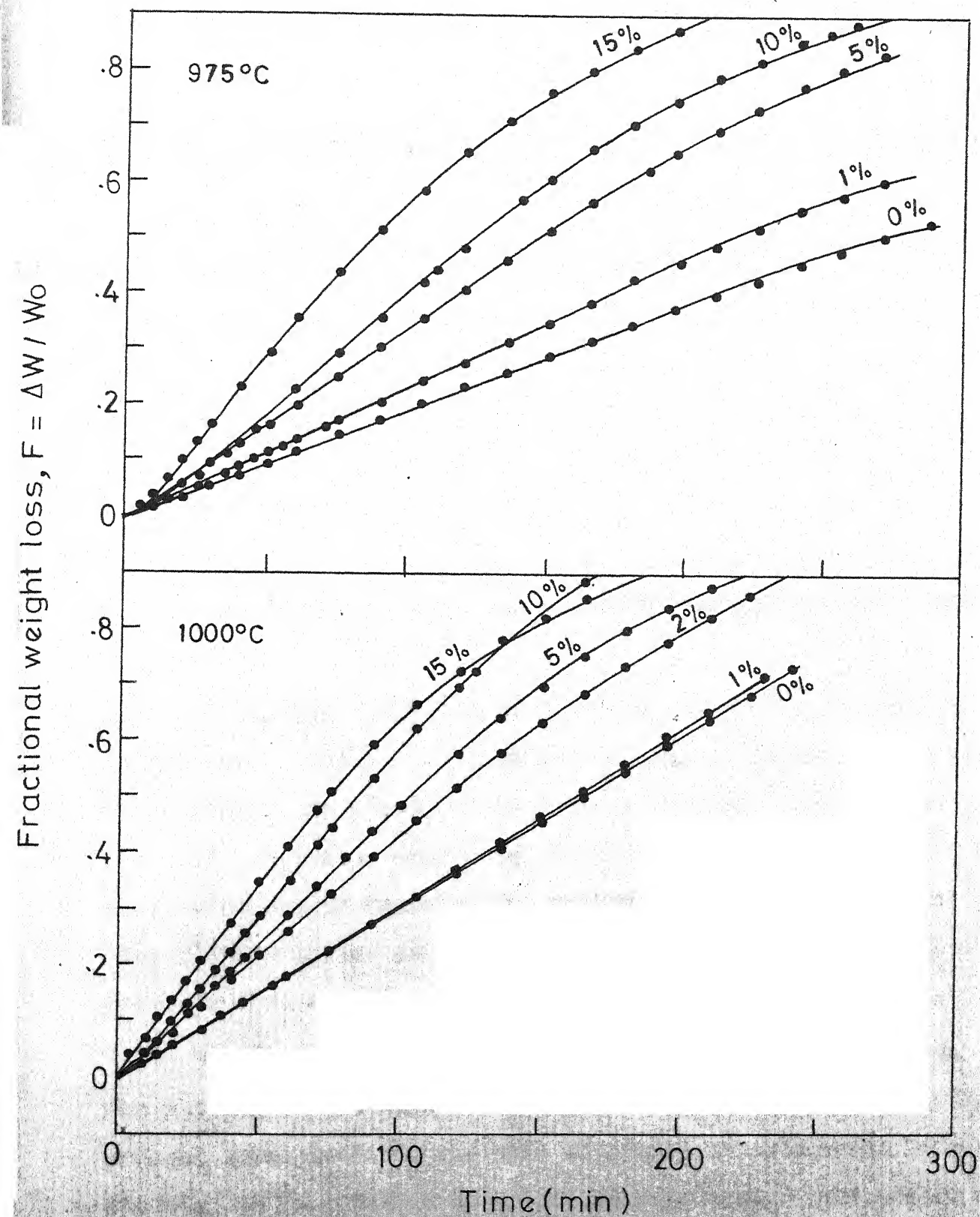


FIG. 4.7 PLOT OF FRACTIONAL WEIGHT LOSS AS A FUNCTION OF TIME FOR CARBON COMPACTS CONTAINING VARYING AMOUNTS OF IRON AT 975 AND 1000°C

The integration of Eq. 4.2 using limits $W=W_0$ at $t=0$ and $W=W$ at $t=t$ gives

$$-\ln \left(\frac{W}{W_0} \right) = R_c t \quad \dots 4.3$$

The experimental data was replotted according to Eq. 4.3 showing $\ln \left(\frac{W}{W_0} \right)$ vs time in Fig. 4.8. It is to be noticed in Fig. 4.8 that the linear behaviour is exhibited only upto 20% carbon burn off. The departure from linear behaviour at higher percentages of carbon burn off is attributed to changes in the porosity and the pore surface area of carbon pellet brought about this reaction. The values of reaction rate per unit mass of carbon per unit time, R_c , could be evaluated from the slopes of the linear segments of plots in Fig. 4.8 and are tabulated in Table IV.2.

An Arrhenius type of plot showing $\log R_c$ vs $1/T$ is shown in Fig. 4.9. The value of activation energy was evaluated from the slope of the curve and is found to be 65.7 kcal/g.mole. This value of activation energy is about 20 kcal/g.mole less than the activation energy reported for carbon gasification reaction.²² This clearly indicates that the transport of gas through the pores is also contributing to the overall rate of reaction.

Discussing the effect of pellet size on pore diffusion Rao & Jalan²⁰ have shown that for the pellet sizes used in the present investigation, the pore diffusion effects would be significant. It is possible to quantitatively analyze the effect of pore diffusion using Thiele⁷⁰ "effectiveness factor", η , which

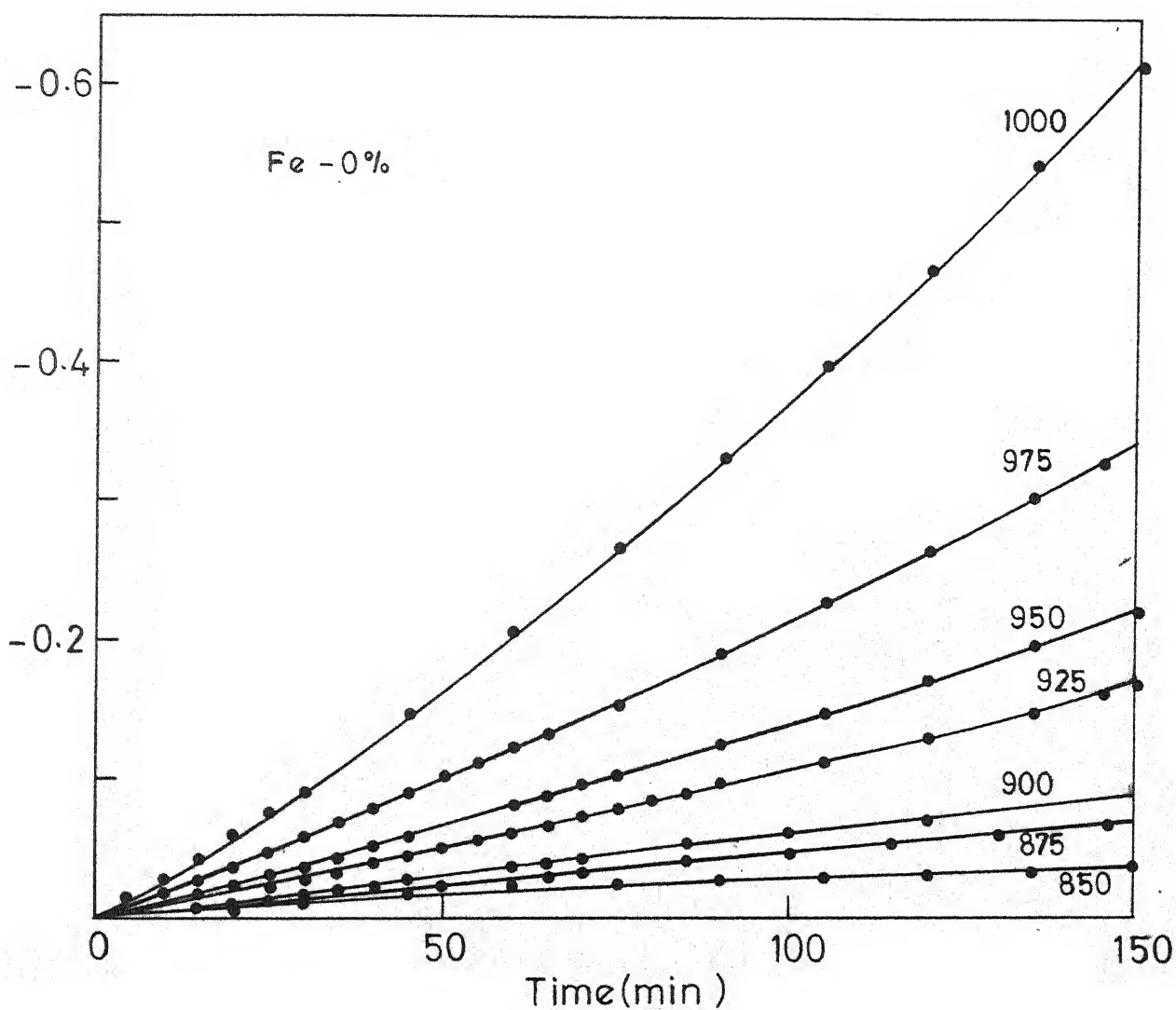


FIG. 4.8 PLOT OF $\ln(W/W_0)$ VERSUS TIME FOR IRON FREE CARBON COMPACT FOR VARIOUS TEMPERATURES (°C)

TABLE IV.2

Rate on Rate Constants and Diffusion Coefficients
at various Temperatures

Temp $^{\circ}\text{F}$	P_2 atm $^{-1}$	P_3 atm $^{-1}$	D_2 cm^2/sec	D_3 cm^2/sec	D_4 cm^2/sec	$R_C \times 10^3$ gm/gm of C-min	$R_{\text{CO}_2} \times 10^6$ gm.mole/ $\text{cm}^3 \cdot \text{sec}$
1123	1120	3.02	0.9534	2.7244	0.0405	0.182	0.3033
1148	960	2.84	0.9959	2.7546	0.0416	0.455	0.7583
1173	620	2.69	1.0285	2.7844	0.0428	0.617	1.0282
1199	350	2.55	1.0615	2.8140	0.0439	1.063	1.7715
1223	214	2.40	1.0949	2.8431	0.0450	1.417	2.3615
1248	125	2.27	1.1287	2.8721	0.0461	2.000	3.3332
1273	80.4	2.16	1.1627	2.9007	0.0472	3.077	5.1281

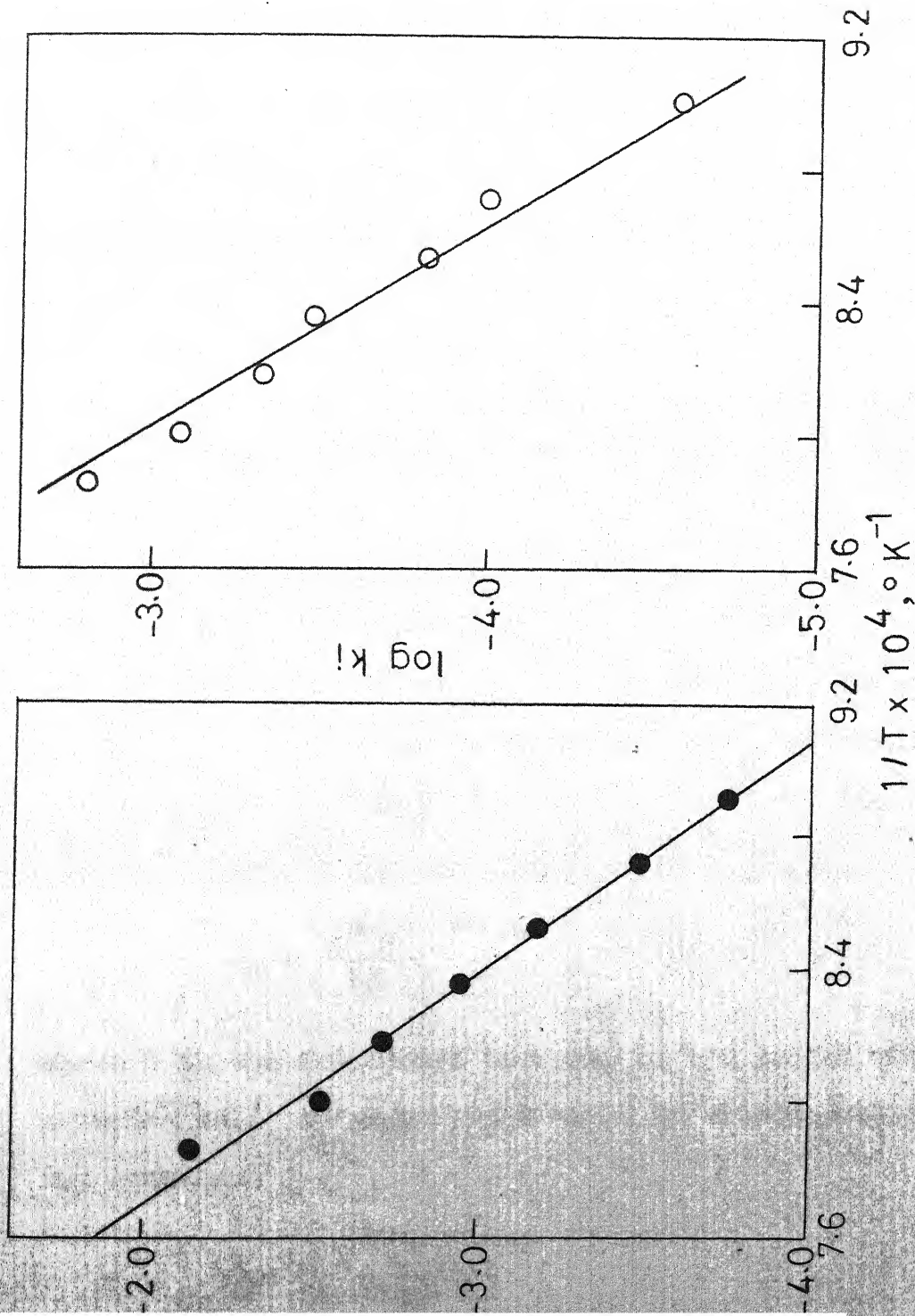


FIG 4.9

FIG. 4.10

PLOT OF $\log R_c$ VERSUS $1/T$ & $\log k_i$ VERSUS $1/T$ FOR IRON FREE CARBON COMPACTS.

is defined as the ratio of the measured reaction rates to the intrinsic rate which could be obtained if the entire pore surface was exposed to the same reactant concentration as the exterior of the pellet. Roberts & Satterfield⁷¹ and Chu and Hougen⁷³ have developed generalized method for evaluating η for complex rate expressions. Roberts & Satterfield⁷¹ have published the values of η for reactions under various conditions in the form of η vs ψ plots, where ψ , the dimensionless modulus introduced by Wagner,⁷⁴ is defined as

$$\psi = \left(\frac{L_p^2 RT}{P_{CO_2} D_e} \right) R_{CO_2} \quad \dots 4.4$$

where L_p is the characteristic dimension of the pellet defined

$$L_p = \frac{\text{Volume of the pellet}}{\text{External surface area of the pellet}} \quad \dots 4.5$$

R_{CO_2} is rate of reaction in gm mole/cm³-s calculated from experimental R_p values listed in Table IV.2. D_e , effective diffusivity could be estimated from Weiss and Swerts⁷⁵ relationship given below

$$D_e = \frac{\theta^2 D}{V_3} \quad \dots 4.6$$

where θ is the fractional porosity of the pellet which could be experimentally measured and D could be obtained from the following equation

$$\frac{1}{D} = \frac{1}{D_k} + \frac{1}{D_b} \quad \dots 4.7$$

In the above equation η_k is the Knudsen diffusivity defined as

$$\eta_k = \frac{2}{3} r \left(\frac{8RT}{\pi M_{CO_2}} \right)^{1/2}$$

$$= 9.7 \times 10^3 r \sqrt{\frac{T}{M_{CO_2}}} \quad \dots 4.8$$

where r is the pore radius which is assumed to be $1/3$ of particle radius^{20 76} and M_{CO_2} is the molecular weight of CO_2 .

The bulk diffusivity η_b could be calculated from the Gilliland equation⁷⁷

$$\eta_b = 0.0043 \frac{T^{3/2} \left(\frac{1}{M_{CO}} + \frac{1}{M_{CO_2}} \right)^{1/2}}{P_t (v_{CO}^{1/3} + v_{CO_2}^{1/3})^2} \quad \dots 4.9$$

where P_t is total pressure (1 atm in this case). v_{CO} and v_{CO_2} are molecular volume of CO and CO_2 respectively and have values 30.7 and 34.0 respectively.

Knowing the values of L_c , D_e , R_{CO_2} and using Eq. 4.4 values of ψ for different experimental conditions could be obtained. ψ values along with the values of various parameters required for evaluation of η values are tabulated in Table IV.3.

The plot of effectiveness factor, η , as a function of modulus ψ , originally drawn by Roberts and Satterfield⁷¹ is reproduced in Fig. 4.11. The plot is given for various i_2 values where i_2 is defined as²⁰

$$i_2 = (I_2 - 1.6 I_2) / (1 + 1.6 I_2) \quad \dots 4.10$$

TABLE IV.3

Intrinsic Rate Constants and Parameters Required for
for their evaluation at various temperatures

Temp $^{\circ}\text{C}$	$\log k_1$	ψ	η	$k_1 \times 10^6$ gm.mole/cm ³ .sec	$k_1 \times 10^6$ gm.mole/gm of O-sec
1123	-0.996	0.019	0.75	0.4044	26.933
1146	-0.997	0.045	0.52	1.4583	98.581
1173	-0.996	0.080	0.45	2.2849	156.744
1198	-0.994	0.103	0.37	4.7876	313.231
1223	-0.990	0.137	0.35	6.7471	476.032
1248	-0.984	0.193	0.30	11.1167	800.526
1273	-0.976	0.295	0.25	20.5124	1500.482

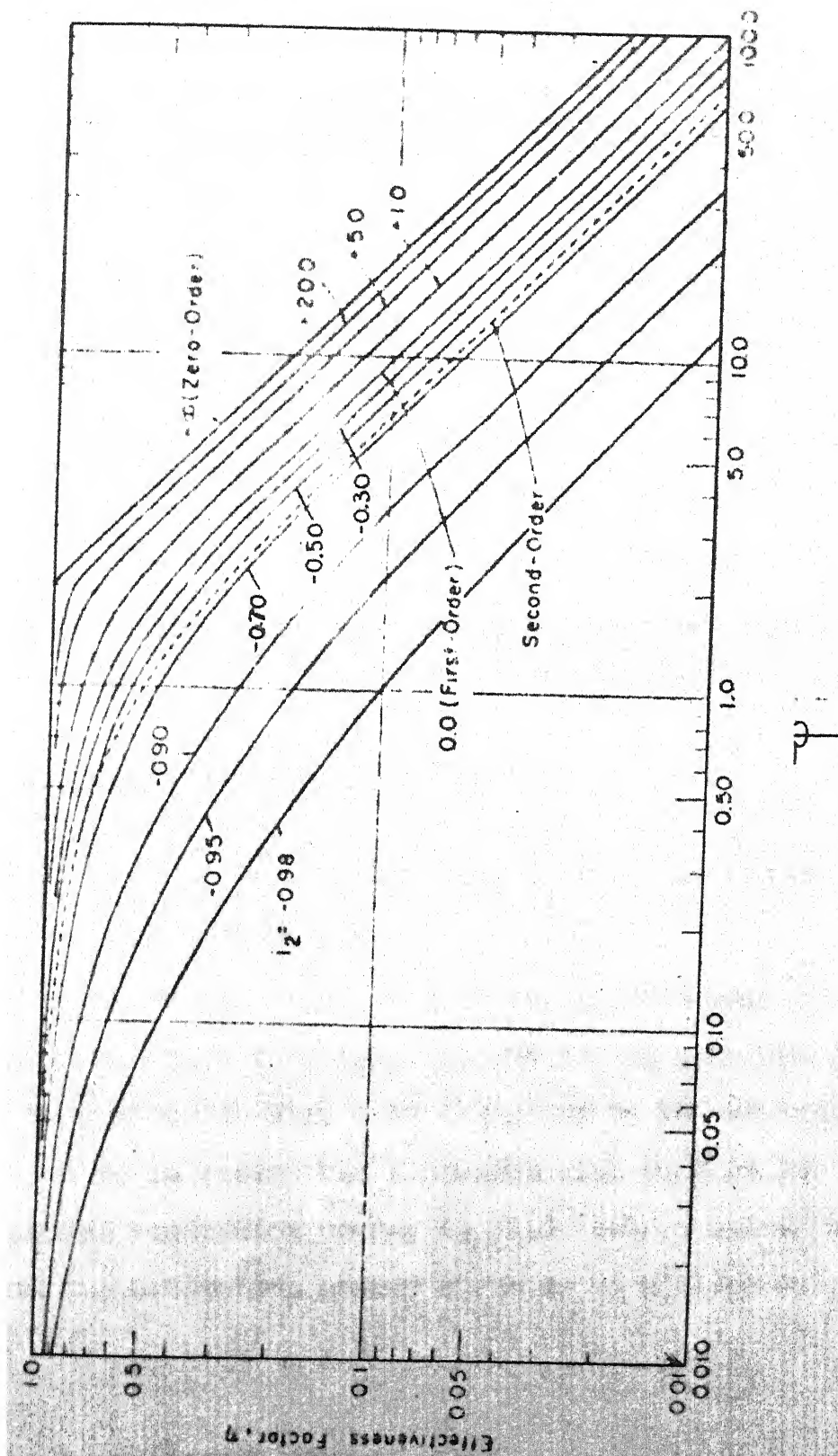


FIG. 4.11 EFFECTIVENESS FACTOR, η , AS A FUNCTION OF MODULUS ψ .
(Taken from Roberts and Satterfield⁷¹)

The values of intrinsic rate constants I_2 and I_3 were taken from literature.³⁰ Plots of I_2 and I_3 versus temperature are shown in Figs. 4.12 and 4.13, respectively. Knowing I_2 and ψ values, values of η could be read from Fig. 4.11 for various experimental conditions. These values are tabulated in Table IV.3.

The values of intrinsic rate of carbon gasification, R_1 gm mole/cm³-sec., could be evaluated from known R_{CO_2} and η values

$$R_1 = \frac{R_{CO_2}}{\eta} \quad \dots 4.11$$

Using Ergun's³³ formulae Rao & Jalan³⁰ obtained following relationship for gasification of carbon in pure CO₂ gas at 1 atm. pressure

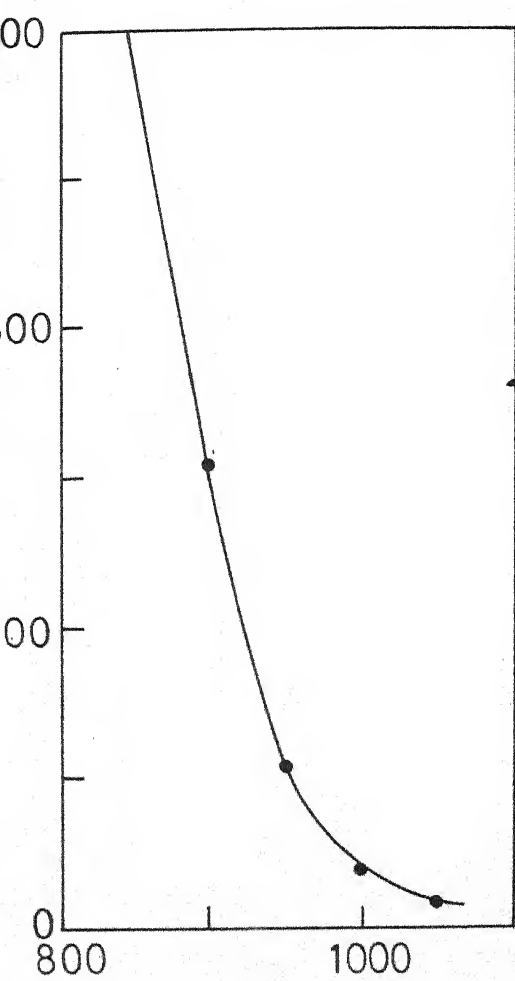
$$\left(\frac{60}{1.2}\right) R_1 = k_1 / (1 + 1/I_3) \quad \dots 4.12$$

Using Wu's³⁰ data for I_3 values, k_1 values were evaluated and are tabulated in Table IV.3.

The activation energy for carbon gasification reaction as visualised by Ergun (Eq. 2.8) was determined from the plot of $\log k_1$ vs $\frac{1}{T}$ shown in Fig. 4.10 and found to be 75 kcal/gm mole. This value is in reasonable agreement with that of Rao and Jalan,³⁰ who reported activation energy as 79.6 kcal/gm mole. Walker et al. reported the activation energy value as 86 kcal/gm mole.

4.2 CATALYTIC EFFECT OF IRON

Catalytic effect of iron on C-CO₂ reaction. The basic data



Temp (°C)

FIG. 4.12

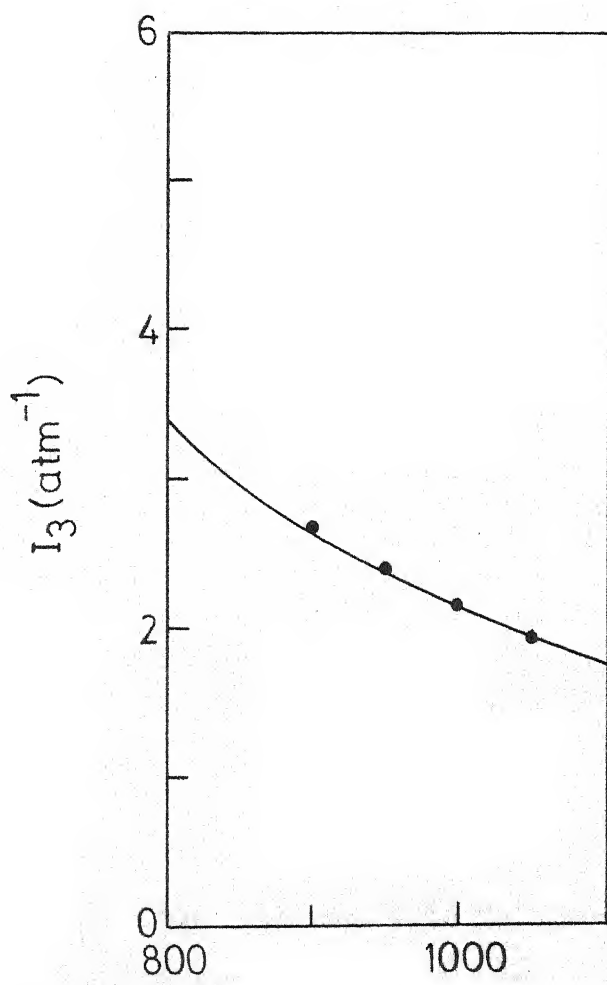


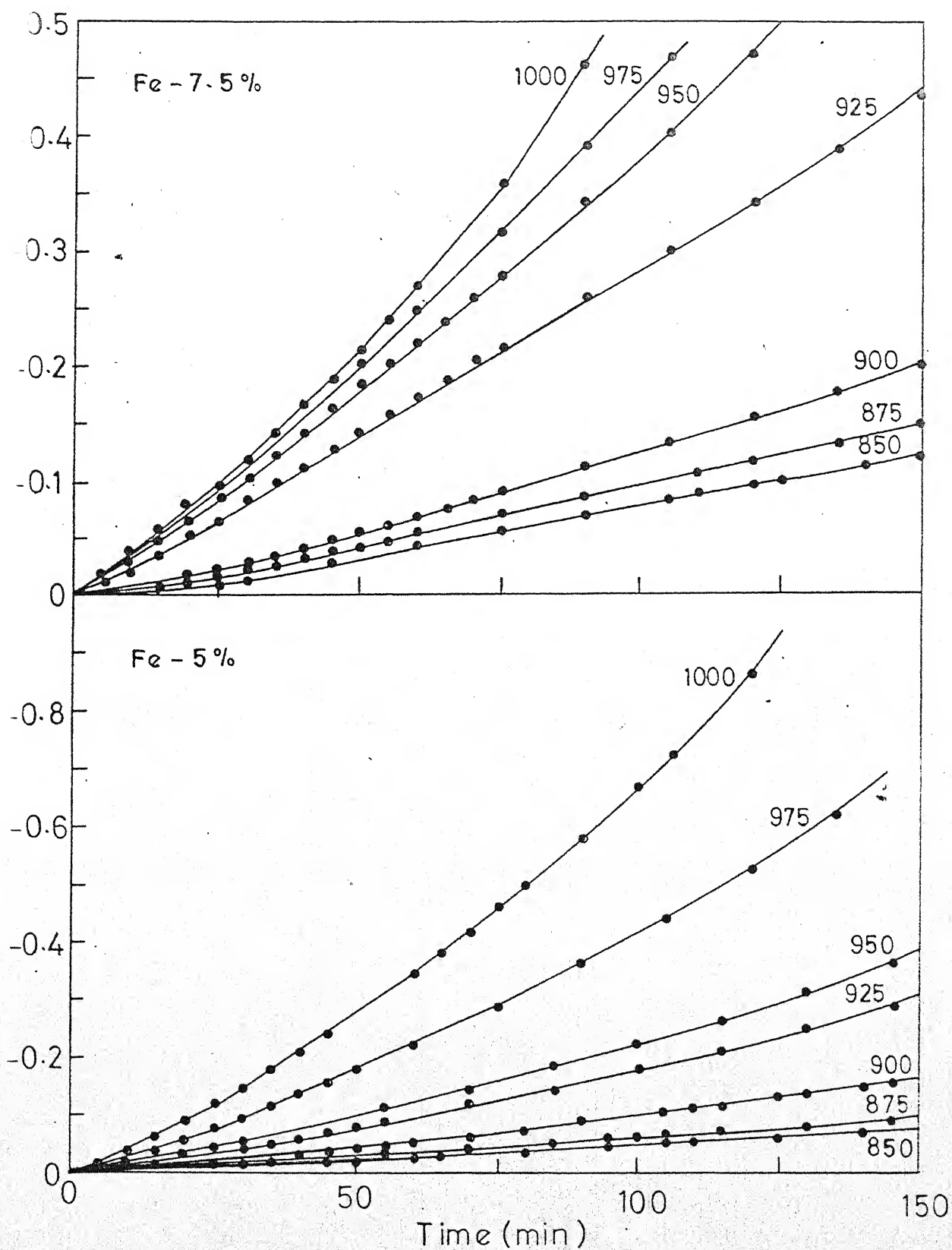
FIG. 4.13

PLOT OF INTRINSIC CONSTANTS I_2 VERSUS TEMPERATURE
AND I_3 VERSUS TEMPERATURE³⁰

varying amounts of iron at regular intervals of time. Fig. 4.2 to Fig. 4.4 are the plots of fractional weight loss versus time at several temperatures ranging from 850 to 1000°C for iron contents varying from 1 to 15%. These plots basically show the effect of temperature on the kinetics of the reaction for a fixed iron content in the carbon compact. The nature of the curves is similar to the nature of the curve obtained for iron free carbon compacts. The effect of temperature for iron containing carbon compacts is similar to that of iron free carbon compacts already discussed earlier. Somewhat unusual behaviour for the compacts containing 2% iron (Fig. 4.2) is attributed to experimental error and to the fact that these runs were carried out using CO_2 gas from a different cylinder.

Figures 4.5 to 4.7 are the plots of fractional weight loss versus time for carbon compacts containing iron contents from 0 to 15% at fixed temperatures. The catalytic effect of iron on the kinetics of C-CO_2 reaction is quite evident. It should, however, be noticed in the plots of Fig. 4.5 and 4.6 there is in fact an increase in weight of the compact in the beginning of the reaction. This effect is quite predominant in the case of compacts containing higher amounts of iron, namely, 10 & 15%. This initial increase in weight is attributed to oxidation of iron by CO_2 . This is also supported by visual examination of some of the partially reacted compacts which were taken out after carrying out the reaction for 15 minutes to 30 minutes.

Plots of $\ln \left(\frac{W}{W_0} \right)$ versus time for compacts containing 5 & 7.5 % iron contents at several temperatures are shown in Fig. 4.14.



3.4.14 PLOT OF $\ln(W/W_0)$ VERSUS TIME FOR 7.5 AND 5% IRON IN CARBON COMPACTS FOR VARIOUS TEMPERATURES

It is to be noticed that only for the initial stages of the reaction, the plots are linear. For reaction time about an hour or so deviation from the linear behaviour starts. Similar plots, though not shown here, have been obtained for other compositions, as well. The values of the rate constants have been evaluated from the linear portion of the curves for various compositions at different temperatures. These are reported in Table IV.4. Figure 4.15 is a plot of rate constant, R_c (gm/gm of C-min) as a function of iron content in the compact at various temperatures. It is to be noticed that the rate constant at a given temperature increases more or less linearly with the increasing iron content. Similar observations have also been reported by Turkdogan and Vinters.⁵³

The effect of iron content on the activation energy was examined by estimating the activation energy values from the Arrhenius type of plots of $\log R_c$ versus $1/T$ for various compositions (Fig. 4.16). Activation energy values are reported in Table IV.4. Figure 4.17 is a plot of activation energy versus iron content in the carbon compact. It is evident from the figure that there is a rapid decrease in activation energy for initial additions of iron. For instance the value of activation energy of 65.7 kcal/gm mole for iron-free compact is brought down to 47.6 kcal/gm mole for carbon compact containing 1% iron. Decrease in activation energy with increasing iron content beyond 1 per cent is more or less linear. The catalytic effect of iron on the rate of C- CO_2 reaction is therefore evident. These observations are in conformity with those of Nakazawaki who has also reported that the reactivity of graphite increases with iron concentration

TABLE IV.4

Rate Constants and Activation Energy values

Iron Composition	RATE CONSTANT k_p , gm/gm of C-min						Activation Energy kcal./gm.mole
	850	875	900	925	950	975	1000
0%	0.000182	0.000455	0.000617	0.001063	0.00142	0.00200	0.00307
1%	0.00036	0.0005	0.0008	0.0012	0.0017	0.0024	0.0033
5%	0.0005	0.00062	0.00102	0.0014	0.0019	0.0037	0.0042
10%	0.00065	-	0.0010	0.0033	-	0.0045	0.0060
15%	-	0.0017	0.00267	0.00486	-	0.0065	0.0075
							65.7
							47.6
							43.02
							35.24
							25.63

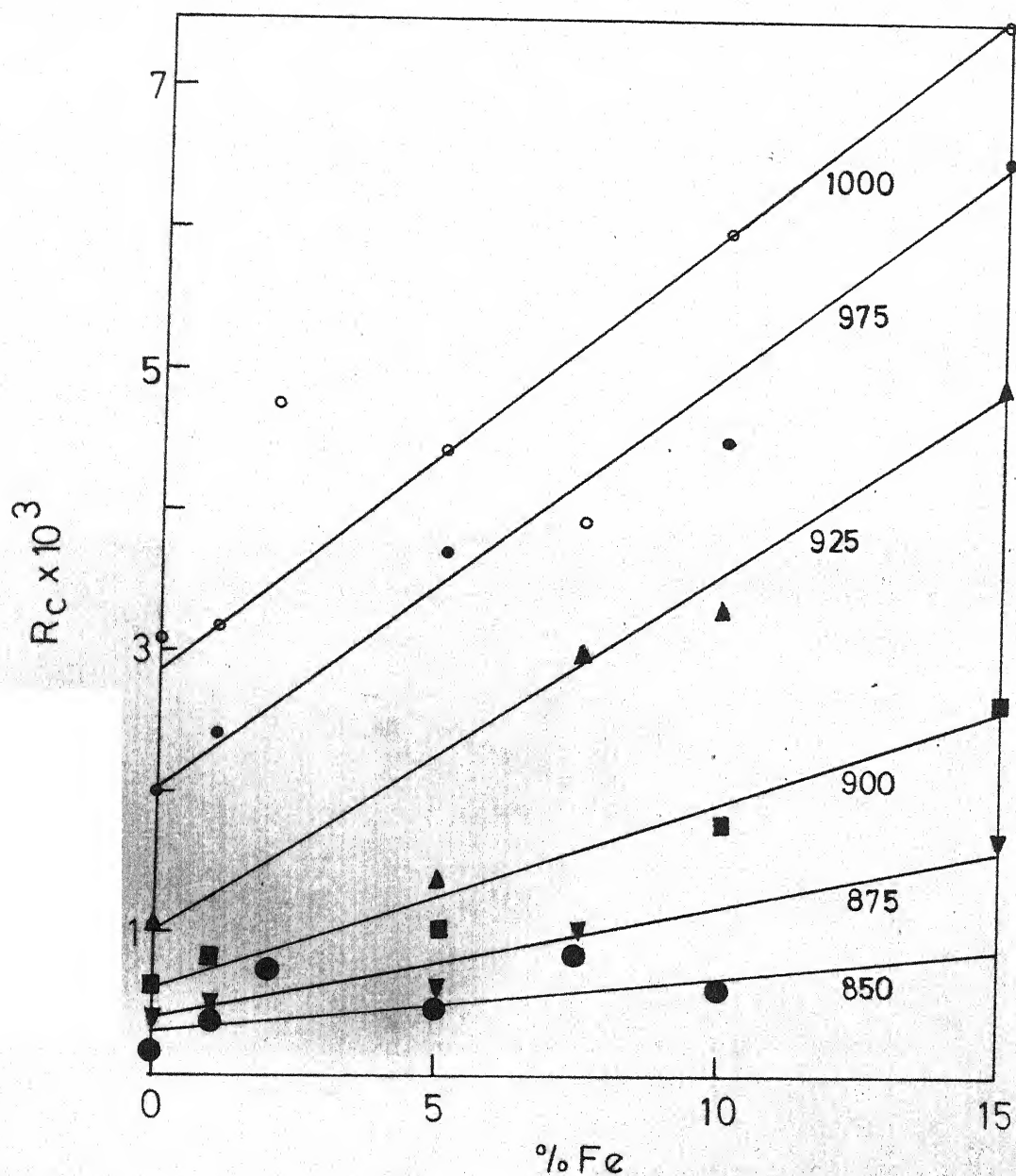


FIG 4.15 PLOT OF R_c VERSUS IRON CONTENT IN THE CARBON COMPACT AT VARIOUS TEMPERATURES ($^{\circ}C$)

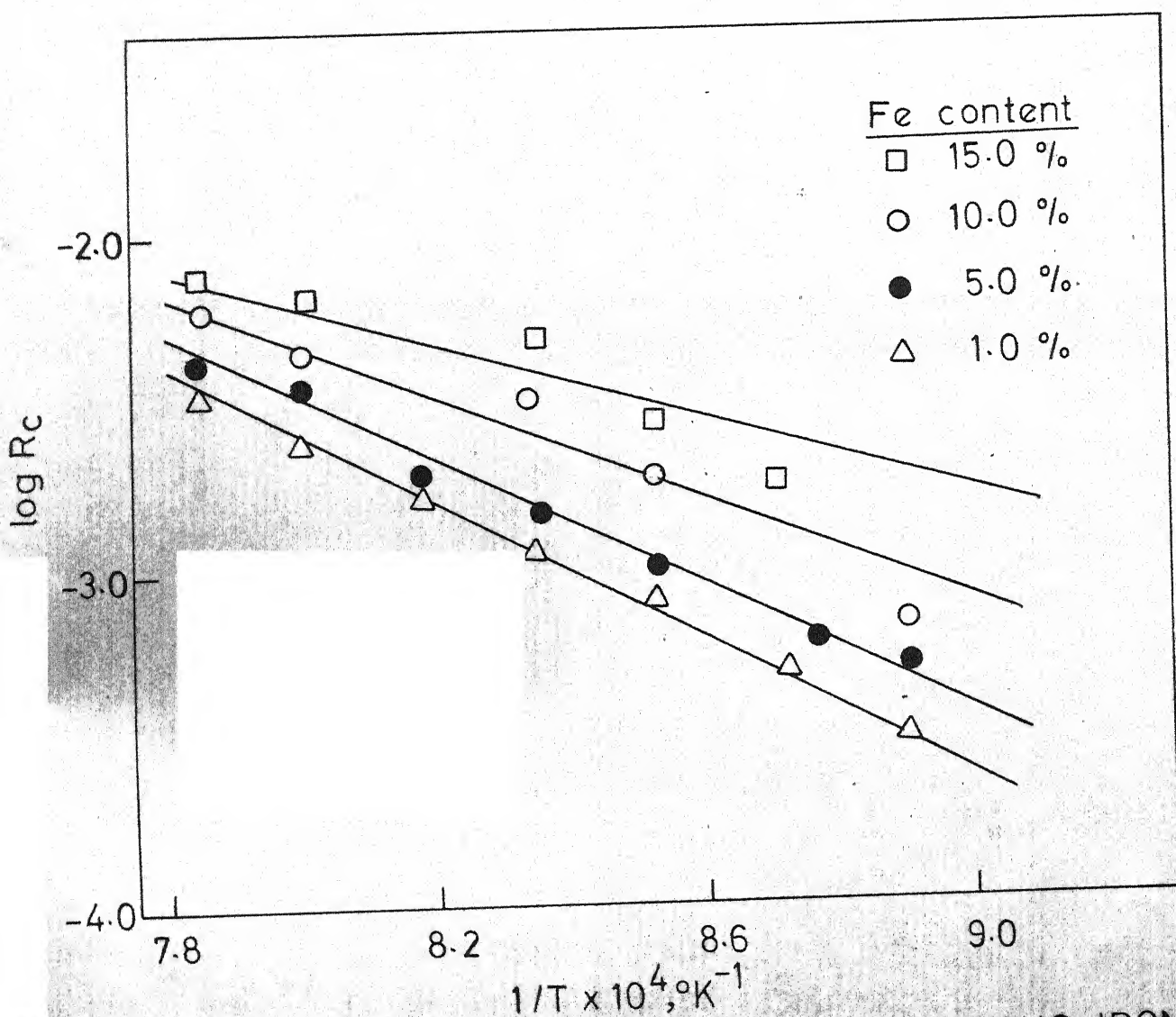


FIG. 4.16 PLOT OF LOG R_c VERSUS $1/T$ FOR VARYING IRON CONTENT IN THE CARBON COMPACTS

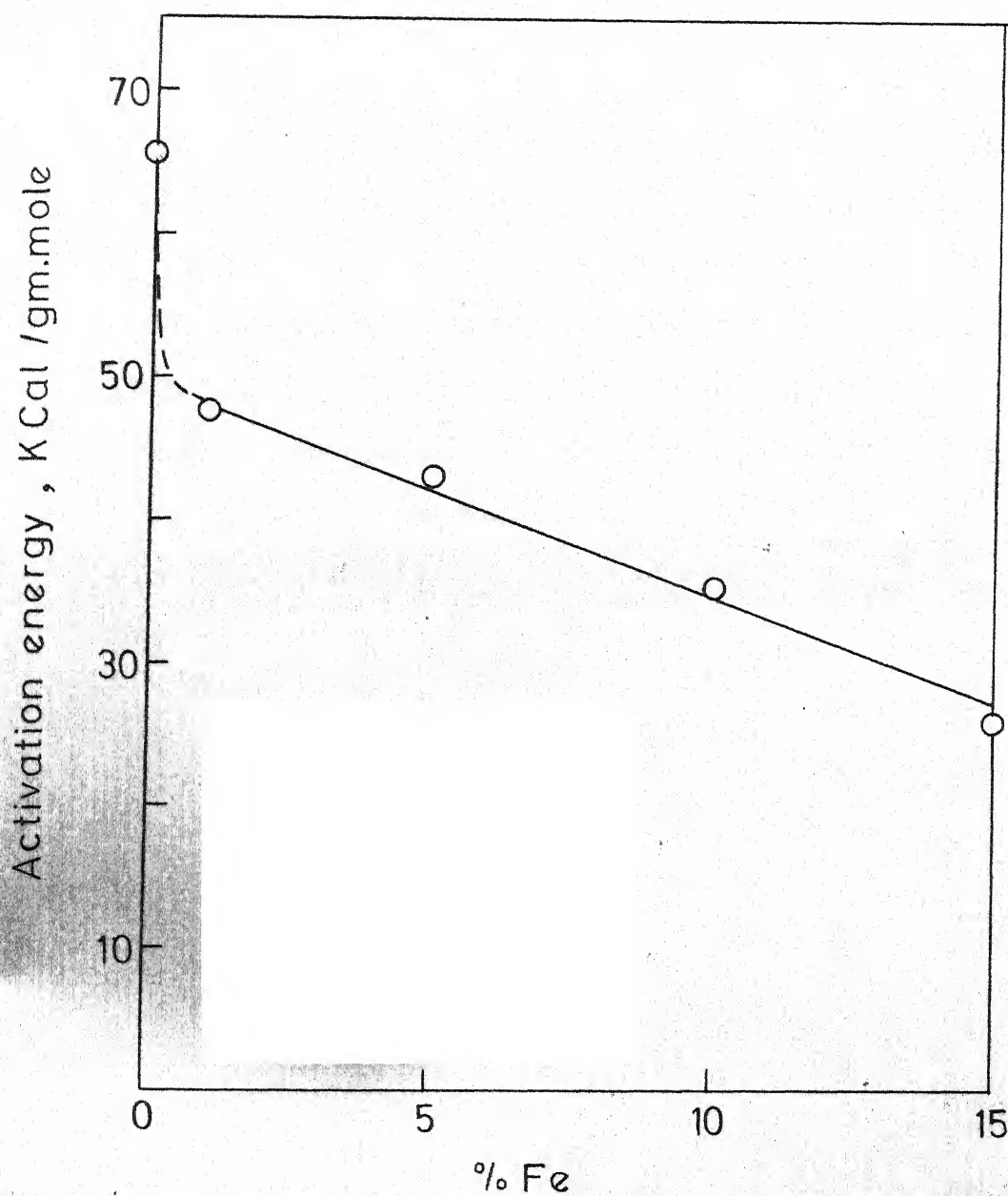


FIG.4.17 PLOT OF ACTIVATION ENERGY VERSUS IRON CONTENT IN THE CARBON COMPACTS

upto about 0.5 weight per cent. The addition of higher concentrations results in only a relatively small further increase in the reactivity.

Regarding the mechanism of the catalysis, although nothing conclusive can be said at this stage, the oxidation of iron in the initial stages does indicate that intermediate compound theory of catalysis operates atleast to some extent. According to this theory, as mentioned earlier also, the catalytic action in C-CO₂ reaction is due to formation of intermediates which serve to oxidise carbon in the vicinity and in the process they return to their original state only to be reconverted by the oxidizing gas (CO₂) to the active intermediate.

CHAPTER - Y

CHAPTER V

SUMMARY AND CONCLUSION

The kinetics of carbon-carbon dioxide reaction and the effect of iron as a catalyst on this reaction has been investigated. Carbon compacts prepared by pressing carbon powder at a pressure of 6000 psi were reacted with carbon dioxide in a wire wound furnace at several temperatures ranging from 850° to 1000°C. To study the effect of iron on this reaction carbon compacts containing varying amounts of iron (1 to 15%) were prepared and reacted with CO₂ in similar manner. The basic data consist of measuring weight loss of the compacts in CO₂ atmosphere at regular intervals of time.

The main results and conclusions of this investigation are as follows:

- (1) The rate of iron free carbon compacts with CO₂ increases with increasing temperature.
- (2) The kinetics of the reaction is controlled both by the transport of gas through the pores and the gasification reaction at pore surface.
- (3) The activation energy value of the gasification reaction evaluated after taking into account the effect of transport steps is found to be 75 kcal/gm mole which is close to activation energy value (~ 80 kcal/gm mole) for this reaction reported in literature.

(4) Iron enhances the rate of $\text{C}-\text{CO}_2$ reaction at all temperatures studied in this investigation.

(5) It is observed that the activation energy for the reaction decreases with increasing iron content. It is, however, noticed that the reduction in activation energy is rather rapid for initial additions of iron. On further additions of iron beyond 1 % the reduction in activation energy is more or less linear.

(6) Although no definite conclusion could be drawn regarding the mechanism of the catalytic effect, the intermediate compound mechanism seems to be more plausible.

APPENDIX

TABLE A-1

Weight Loss Data for Varying Iron Content
in the Carbon Compacts at 850°C

Time (min)	ΔW (in mg)						
	Iron composition						
	0%	1%	2%	5%	7.5%	10%	15%
5	3	1	2	-1	-7	-17	-23
10	5	3	4	0	-5	-30	-27
15	7	5	6	2	-1	-28	-23
20	9	7	12	5	4	-24	-20
25	11	8	16	8	6	-20	-15
30	13	10	20	10	13	-17	-10
35	14	13	24	12	17	-12	-6
40	16	15	27	14	21	-9	-2
45	18	17	31	16	25	-5	3
50	19	20	35	18	29	-2	8
55	21	22	38	21	34	1	13
60	23	25	42	24	39	5	18
75	26	32	53	32	52	16	43
90	29	38	64	40	63	26	57
105	30	46	75	48	76	35	61
120	33	53	82	58	86	45	75
135	36	60	90	66	97	53	88
150	38	67	98	73	108	62	101
165	40	74	108	80	119	72	114
180	42	80	117	86	131	82	127
195	44	87	126	94	141	95	140
210	45	94	135	101	151	104	152
225	47	101	143	108	161	113	165
240	49	108	151	116	171	122	176
255	52	115	158	126	181	130	188
270	54	122	166	131	192	140	200
285	56	129	174	140	202	147	211
300	58	136	181	147	212	156	223

TABLE A-2

Weight Loss Data for Varying Iron Content
in the Carbon Compacts at 875°C

Time (min)	ΔW (in mg)						
	iron composition						
	0 %	1 %	2 %	5 %	7.5 %	10%	15%
5	2	4	0.5	-6	-4	-20	-22
10	5	6	2	-7	0	-26	-24
15	7	8	4	-4	5	-24	-18
20	9	12	8	-1	10	-20	-12
25	11	14	11	2	15	-15	-4
30	14	17	14	5	20	-11	2
35	16	19	17	8	25	-6	8
40	19	22	20	11	30	-2	16
45	22	24	23	15	35	3	22
50	24	27	26	19	40	9	30
55	26	30	29	22	45	13	37
60	29	32	33	25	50	17	44
75	38	40	44	34	64	31	64
90	46	48	53	43	79	44	87
105	54	56	63	54	92	58	107
120	61	65	72	64	105	72	127
135	68	74	81	73	119	86	146
150	75	83	90	83	132	100	165
165	83	92	98	93	144	114	184
180	90	100	106	103	157	128	203
195	97	108	114	112	167	141	222
210	104	116	121	121	180	155	239
225	111	125	130	130	191	168	256
240	118	134	139	138	203	182	272
255	125	143	147	147	215	196	287
270	132	151	156	156	227	210	302
285	139	160	165	166	239	224	318
300	146	169	174	175	251	238	333

TABLE A-3

Weight loss data for Varying Iron Content
in the Carbon Compacts at 900°C

Time (min)	ΔW (in mg)						
	Iron composition						
	0 %	1 %	2 %	5 %	7.5 %	10%	15%
5	2	4	10	-2	-4	-4	-23
10	5	9	17	1	-1	-11	-22
15	10	13	24	5	5	-6	-13
20	12	17	31	10	13	2	-3
25	15	21	42	15	20	10	10
30	18	26	50	20	26	18	22
35	21	31	58	26	32	26	34
40	25	35	65	31	39	35	46
45	28	40	73	37	45	43	58
50	32	45	80	42	52	52	71
55	35	49	87	47	58	61	82
60	39	53	94	53	64	71	95
75	48	66	115	69	83	97	130
90	57	80	136	86	102	112	165
105	66	93	156	104	121	148	197
120	75	106	176	121	140	174	229
135	84	119	196	138	158	199	259
150	93	132	214	154	176	222	288
165	102	145	232	169	194	246	316
180	111	157	250	186	212	270	342
195	120	169	267	201	229	293	366
210	130	181	284	216	245	316	389
225	139	193	301	231	262	339	410
240	149	205	317	246	278	361	440
255	159	216	333	261	294	374	454
270	168	227	349	276	310	405	475
285	178	238	365	291	326	429	496
300	188	249	380	306	341	449	514

TABLE A-4

Weight Loss Data for Varying Iron Content
in the Carbon Compacts at 925°C

Time (min)	ΔW (in mg) in composition						
	0 %	1 %	2 %	5 %	7.5 %	10%	15%
5	6	3	6	-4	6	-10	-20
10	11	9	12	1	19	-7	-12
15	15	16	19	9	34	3	3
20	20	24	26	19	48	17	22
25	24	31	33	28	62	32	41
30	30	38	39	37	76	45	59
35	36	45	46	46	88	59	80
40	43	53	53	55	100	73	95
45	48	61	61	64	112	88	113
50	53	69	69	73	124	102	130
55	59	76	76	83	136	116	148
60	65	83	84	93	148	131	166
75	82	105		122	182	173	211
90	98	125		151	214	213	257
105	114	146		180	243	256	304
120	130	167		209	273	286	348
135	146	185		239	302	337	391
150	159	204	216	268	331	378	428
165	178	221	238	297	359	418	464
180	194	241	261	327	384	458	500
195	209	262	283	356	410	495	536
210	225	283	306	385	435	532	567
225	240	304	328	414	460	567	597
240	255	325	350	442	484	597	625
255	271	345	370	469	507		
270	286	366	391	498	528		
285	301	386	401	526	548		
300	316	407	421	553	568		

TABLE A-5

Weight Loss Data for Varying Iron Content
in the Carbon Compacts at 950°C

Time (min)	ΔW (in mg)						
	Iron composition						
	0 %	1 %	2 %	5 %	7.5 %	10%	15%
5	6	6	5	-4	12	-10	-13
10	12	15	12	4	25	-2	-17
15	18	24	20	13	42	21	-2
20	24	32	29	23	59	41	13
25	32	40	38	33	75	62	36
30	38	48	46	44	91	82	65
35	45	56	55	54	106	102	95
40	53	65	64	66	121	123	123
45	61	74	73	78	138	144	149
50	68	84	82	89	153	166	174
55	75	92	91	100	167	186	198
60	83	100	100	111	181	205	222
75	104	126	128	143	224	267	291
90	125	152	155	179	265	328	370
105	146	177	183	213	306	388	443
120	167	202	211	247	345	448	508
135	188	227	238	284	383	503	559
150	209	252	268	319	420	553	605
165	230	278	298	354	456	601	646
180	251	303		391	491	646	678
195	272	329		427	526	687	
210	293	353		464	559	722	
225	314	380	447	500	591	756	
240	335	404		537	621		
255	356	427		573	649		
270	377	451		608	675		
285	398			644			
300	419			679			

TABLE A-6

Weight Loss Data for Varying Iron Content
in the Carbon Compacts at 975°C

Time (min)	ΔW (in mg)						
	Iron composition						
	0 %	1 %	2 %	5 %	7.5 %	10 %	15%
5	9	8	17	6	10	4	16
10	18	17	36	21	23	13	34
15	28	27	56	38	40	28	59
20	38	37	77	55	56	47	85
25	48	47	97	72	73	67	116
30	59	58	116	89	92	87	144
35	70	68	136	106	109	107	172
40	81	79	156	123	126	127	200
45	92	90	176	140	143	147	228
50	102	101	195	157	159	170	253
55	112	112	213	173	177	193	278
60	122	124	231	190	194	217	302
75	152	159	287	241	244	277	373
90	183	195	340	292	295	337	440
105	215	231	392	343	345	397	499
120	246	267	442	392	395	456	555
135	276	303	490	443	443	516	604
150	307	339	535	492	490	571	646
165	337	375	578	543	535	621	683
180	367	410	618	585	578	663	714
195	396	445	655	625	619	703	740
210	425	489	690	663	658	740	760
225	453	522		701	695	774	
240	481	554		738	731	802	
255	508	586		769	765	827	
270	536	617		797	796		
285	567	647			825		
300	589	675			852		

TABLE A-7

Weight Loss Data for Varying Iron Content
in the Carbon Compacts at 1000°C

Time (min)	ΔW (in mg)						
	Iron composition						
	0 %	1 %	2 %	5 %	7.5%	10%	15%
5	15	12	34	18	13	18	29
10	27	27	47	40	28	39	57
15	41	42	69	65	46	61	85
20	55	56	91	89	67	85	114
25	69	73	113	114	87	130	142
30	83	89	136	139	106	152	171
35	99	105	159	166	126	184	202
40	114	121	182	191	147	215	231
45	130	138	205	216	167	247	259
50	146	154	228	241	187	279	287
55	162	171	251	267	207	310	314
60	177	187	274	292	228	341	341
75	223	236	343	369	293	433	425
90	269	285	410	442	359	520	496
105	313	336	477	513	423	602	555
120	355	384	541	582	486	678	607
135	399	433	602	645	547	701	650
150	440	481	659	703	604	748	687
165	480	528	713	757	658	806	719
180	524	575	764	805	707	866	743
195	567	621	812	845	752	926	760
210	609	665	857	882	791	932	772
225	651	708	898	913	826	935	780
240			933	938		936	785
255				956		936	
270				970			

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